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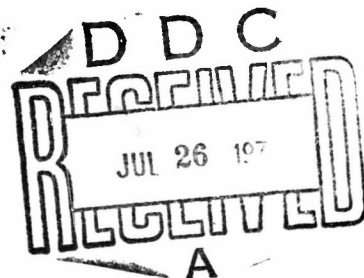


THERMAL DECOMPOSITION AND COMBUSTION OF EXPLOSIVE SUBSTANCES

(Selected Chapters)

by

K. K. Andreyev



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К. К. АНДРЕЕВ

Термическое разложение
и горение
взрывчатых веществ

ИЗДАНИЕ ВТОРОЕ
(ПЕРЕРАБОТАННОЕ И ДОПОЛНЕННОЕ)



ИЗДАТЕЛЬСТВО «НАУКА»
МОСКВА - 1966

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U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

* ye initially, after vowels, and after ъ, Ъ; e elsewhere.
 When written as ѣ in Russian, transliterate as yě or ѣ.
 The use of diacritical marks is preferred, but such marks
 may be omitted when expediency dictates.

FOLLOWING ARE THE CORRESPONDING RUSSIAN AND ENGLISH
DESIGNATIONS OF THE TRIGONOMETRIC FUNCTIONS

Russian	English
sin	sin
cos	cos
tg	tan
ctg	cot
sec	sec
cosec	csc
sh	sinh
ch	cosh
th	tanh
cth	coth
sch	sech
csch	csch
arc sin	sin ⁻¹
arc cos	cos ⁻¹
arc tg	tan ⁻¹
arc ctg	cot ⁻¹
arc sec	sec ⁻¹
arc cosec	csc ⁻¹
arc sh	sinh ⁻¹
arc ch	cosh ⁻¹
arc th	tanh ⁻¹
arc cth	coth ⁻¹
arc sch	sech ⁻¹
arc csch	csch ⁻¹
<hr/>	
rot	curl
lg	log

Translator's note: On several occasions, symbols found in formulae and calculations appear to have been rendered incorrectly in the original document. They will be shown exactly as they appear in the original.



R. Butler

EDITOR'S COMMENTS

The author of this book - one of the greatest specialists in the field of the theory of explosives - Professor Konstantin Konstantinovich Andreyev, began his scientific activity at the end of the 1920's, while still a student of the Moscow Higher Engineering School.

One of this first works was the investigation of the thermal dissociation of barium azide, carried out by him during 1928-1929 in Berlin, where for about a year he worked as a trainee at the Physicochemical Institute of Berlin University. Somewhat later, at the beginning of the 1930's at the Institute of Chemicophysics in Leningrad, working under the leadership of Yu. B. Khariton, K. K. Andreyev was the first to undertake the examination of the combustion of secondary explosives. Since then, mainly at the Moscow Chemical Technological Institute named after D. I. Mendeleev (at which K. K. Andreyev worked from 1935 until death), he carried out more than 150 works on various questions of the theory of explosives. However, thermal dissociation and the theory of combustion of explosives. However, thermal dissociation and the theory of combustion of explosives always remained the most important and closest to him.

In 1957 the monograph of Professor K. K. Andreyev "Thermal decomposition and the combustion of explosives" appeared. This book rapidly went out of print and was translated into a number of European languages.

The stormy development of investigations in the field of the combustion of explosives in recent years has required the considerable addition to the book of new material and a review of some of its sections. Therefore, in 1963 K. K. Andreyev began the preparation of the book for republication. Much of it was changed, and a large part of the material has been rewritten.

In February of 1964 K. K. Andreyev became ill. During the last months of his life, despite undergoing several operations, he worked, much and intensely on the book, having written more than half again the material introduced into it, and at the end of April, in general, completed this work. K. K. Andreyev passed away on May 9, 1964 at 60 in the full prime of his creative forces.

Despite the fact that a great part of this book in typewritten form was read and verified by Konstantin Konstantinovich, he did not succeed in finishing much of it. About 300 pages arrived for printing in manuscript materials, written although in sufficiently finished form (Konstantin Konstantinovich, as a rule, wrote his works immediately in clean copy, and, subsequently, he usually did not introduce basic changes in them) but, nevertheless, not adjusted and not corrected by the author. The closest students and followers of K. K. Andreyev prepared for press a vast amount of illustrative material, and compiled charts and a bibliography.

In the scientific works of K. K. Andreyev we see the example of the skillful combination of clarity and sequence of scientific thought and the correct choice of the method of investigation and the direct practical application of the obtained results. The problems of the chemical conversion explosive are solved by him allowing for the totality of the many factors capable of affecting the course of the process in certain specific conditions. But if we take into account in this case the unusually wide choice of explosives most interesting in a practical sense, the uniqueness and encyclopedic quality of the given monograph become clear. A description of the physicochemical structure and various forms of conversions of basic

types of explosives and the saturation by factual material make the book an irreplaceable textbook for a wide circle of scientific workers, engineers and students of physicochemical and chemical specialties

The scientific views of K. K. Andreyev is unusually wide. In essence, in each section of the book the basic results and basic facts belong to him personally and to his students. This refers first of all, to the thermal dissociation and theory of combustion of secondary explosives, to the analysis of critical phenomena and the physical essence of the distinction in properties of a number of explosive.

After a description of the basic forms of explosives and their ability toward chemical conversion of a certain type (stable combustion, nonstationary combustion and detonation), to which the first chapter is devoted, the author examines the basic questions of chemical kinetics of the emergence and development of an explosion under the effect of the change in temperature conditions. Despite the completeness and wide reputation of the kinetic scheme of the spontaneous ignition of gases, worked out by N. N. Semenov, D. A. Frank-Kamenetskiy and other Soviet scientists, the description of the dynamics of thermal decomposition of condensed explosives is still far from its completion. Here, there probably should be noted additionally a series of recent works of colleagues of the Institute of Chemical Physics of the Academy of Sciences of the USSR, where calculations of thermal explosion for a number of substances, which can be useful during the analysis of experimental data have been made.

Subsequent chapters are devoted to the description of various forms of "slow" combustion, mainly of condensed substances. The actuality of the systematization of scientific results in this field, many of which belong to the author of the book, is connected with the rapidly growing range of problems of new technology. In sequential form characteristics of the complex physicochemical model of the process of combustion are examined, and this includes, in the form of a continuous connection, both individual characteristics of the

chemical conversion of a selected substance and the effect of physical conditions (temperature, pressure, density, hydrodynamic factors and so on) on the process of the chemical conversion. Especially interesting here are questions of the stability of combustion and transition to detonation in the application to the combustion of powders and other complex condensed systems.

Of course, it does not follow to consider as a deficiency of the great work of the author the absence of such sequential and thorough analysis of the detonation type of the chemical conversion of explosives. This work, with respect to its volume, go far beyond the framework of the project of this book. However, it is impossible not to note the intensely continuing search of a clear physical scheme of detonation combustion. In particular, this refers to the section on condensed explosives, where as yet only the very first steps in the creation of such a scheme are described.

K. K. Andreyev worked extremely thoroughly on everything which he published, and when he managed to prepare a manuscript for publication he undoubtedly would introduce into it several changes and additions. However, those who worked on the book did not consider it possible to change anything in the text written by K. K. Andreyev.

The basic work with the preparation of the manuscript for press was made by B. S. Svetlov (Chapters I and II), A. P. Glazkova (Chapter III) and B. N. Kondrikov (Chapters IV, V and VI).

A. I. Gol'bind took part in the discussion of the questions connected with the preparation of the book for a press.

R. I. Soloukhin

PREFACE

The processes of combustion of condensed substances represent a considerable practical interest. These processes are widely used in technology, mainly in the firearms of different types, in pyrotechnic products, time, inhibitors, Bickford fuse, electric detonators of retarded action and others.

The combustion of explosives can appear also for different reasons at plants and storehouses in the production and storage of explosives and well as during their use.

The prevention of the emergence of a combustion, methods of combatting the outbreak of fire, and the prevention of the transition of combustion into detonation represent one of the most important problems of the providing of safety of production, storage and application of explosives.

The questions of the technical use of the combustion of explosives are discussed in appropriate special manuals [1], and their investigation go beyond the framework of this book.

Together with the practical importance the questions of combustion of explosives represent great theoretical interest. During combustion a chemical reaction occurs at very high temperatures, which are almost inaccessible under other conditions of the conducting of a reaction, with the exception of a detonation. Furthermore, it is

possible to carry out the process also at very great and controlled pressures. Thus, in principle it is possible, by examining the processes of combustion, to study the characteristics of the course of chemical reactions in the indicated uncommon conditions.

Of no less theoretical importance are questions of the stability of combustion of explosives and the conditions of its transition into a detonation. Contemporary explosive technology is based on the existence of three basic classes of explosives: priming, secondary and propellant (powders). The basic distinction between these classes of explosives consists in the different degree of the stability of their combustion.

Despite the great theoretical and engineering interest in the problem as a whole, it has remained until recently almost unstudied. During the last 20 years this gap to a considerable extent has been filled mainly by the works of Soviet scientists according to the investigation of processes of combustion of explosives. These works allowed giving a general picture of the process and building the quantitative theory of combustion, the knowledge of which, undoubtedly, is useful for the investigators working on questions of the technical application of the combustion of explosives.

The majority of works on combustion is published in various physicochemical and physical journals and others, nonperiodic, publications of different profile, the observing of which is difficult. Furthermore, all works are devoted to the individual particular questions of the problem, and there are no works of a survey nature. For these reasons it was expedient to give a summary and generalization of the experimental and theoretical material according to the investigation of the combustion of explosives, which constitutes the task of this book.

The greatest attention in the book is given to experimental works of the recent period conducted under conditions which allow using results of an experiment as material for the creation of a theory and check of it. The numerous investigations conducted mainly

on powders at the end of the last and in the current century for the solution of technical problems of barrel artillery, are touched upon in a small degree, especially as these works, as well as conclusions of them, are more or less discussed in detail in a number of monographs on interior ballistics.

The book includes six chapters. The first chapter is devoted to the general characteristic of basic forms of the chemical conversion of explosives and to main types of explosives, according to composition, chemical structure and capability of stable combustion, and also to detonation.

In the second chapter the slow chemical conversion of explosives under the effect of increased temperature is examined.

The part of this chapter which in the first publication was devoted to general questions of chemical kinetics, in this publication it is absent, inasmuch as these questions were recently examined in detail in a whole series of monographs [2-5]. The chapter gives experimental data on the thermal dissociation of the basic representatives of different classes of explosives - nitroesters, nitrocompounds of aromatic and aliphatic series, solid explosives (picrates, styphnates, azides, perchlorates). This section of the chapter is substantially supplemented and modernized on the basis of the large number of works carried out and published in recent years in Soviet and foreign literature. In conclusion a generalization of the examined data and tables of basic dynamic characteristics of various explosives.

In the third chapter experimental data on the stable combustion of explosives are discussed. It starts with a description of various methods of the investigation (bombs of variable and constant pressure). Further critical conditions of combustion are examined: critical diameter, temperature and pressure. These questions recently acquired great importance especially in connection with the burning of industrial explosives, and therefore the section is substantially supplemented by actual and theoretical data. Dependences of the rate of combustion

upon pressure, initial temperature and cubic density are further successively described for basic explosives. Data for individual explosives are greatly reduced, and the reader is referred to the first publication where they are examined in detail. The composition of gas products of combustion and experimental data by definition of its temperature are briefly examined.

In the fourth chapter the basic theories of combustion - Michelson and Mallard - Le Chatelier, Zel'dovich - Belyayev are examined, and a correlation of experimental data with conclusions of the theory in reference to various types of explosives (volatile, nonvolatile, quick-burning) is produced.

In the fifth chapter an account is given of the theory of the stability of combustion, experimental data on this question and the correlation of these data with the theoretical conclusions in reference to the combustion of solid, powdery and liquid explosives.

In the sixth chapter specific cases - detonation and combustion of explosives in various conditions (intense heating, effect of light and others) are examined.

The book is intended for investigators working in various fields of the technical use of the combustion of explosives, for workers of factories producing explosives and powder, and for specialists in mining and blasting. It can be used also as a training manual for students of advanced courses of appropriate specialties.

K. K. Andreyev

CHAPTER I

GENERAL CHARACTERISTICS OF EXPLOSIVES AND BASIC FORMS OF THEIR CHEMICAL CONVERSION

Explosives, just as nonexplosive substances, are capable of a slow chemical conversion. This form of the course of chemical reaction does not indicate basically the fundamental characteristics which would be peculiar only to [VV] (BB) explosives.

A characteristic distinction of **explosives** is their ability toward chemical conversion in two different forms - combustion and detonation. In contrast to the slow chemical conversion occurring more or less evenly in the whole volume of explosives, with combustion and detonation there appears the front of the conversion - the zone of intense chemical reaction, which separates the unreacted substance from the products of reaction and moves in explosives.

The basic formal distinction between combustion and detonation is in the magnitude of linear velocity of propagation of the front of the conversion, measured for typical explosives in millimeters per second with combustion and kilometers per second with detonation.

One of the basic consequences of the high velocity of propagation of a reaction at detonation is the emergence of extremely high and rapidly increasing pressure produced by gas products of the conversion into the environment. As a result of the formation of the difference in pressures between the products of detonation and environment, the potential energy of products of detonation in usual conditions of the course of the latter is transformed into mechanical

work. In this case, since the magnitude of pressure is very great (of the order of hundreds of thousands of atmospheres), then the work being accomplished by gases upon detonation, referred to a unit of time, in other words, power, is extremely great and more than that for all other standard sources of work. Exceptionally great power, easily attainable with detonation, constitutes the basis of its technical use.

In the combustion of explosives (in the absence of a shell) as a result of the slowness of the formation of gases, the increase in pressure is highly insignificant, and mechanical action is practically absent.

The ability to detonate is most specific for explosives not only in essence of the mechanism of the process, but also according to the external picture of its flow and action. The combustion, as is known, is observed in systems not able to detonate (the combustion of any fuel in air), and externally its flow in these systems is very similar to the combustion of explosives. A considerable distinction consists in that the combustion of nonexplosive substances, as a rule, requires the inlet of air or other gas which takes part in the reaction, the admission of which to a considerable degree determines the flow of combustion. The combustion of explosives occurs without the participation of the environments. In essence the application of the same term "combustion" to both processes is determined only by their external similarity, and it would be more correct to designate the combustion of explosives differently, for example, as an "independent" combustion.

In order that the chemical conversion could occur in the form of a combustion and detonation, it should be exothermic and proceed at high speed, the products of a conversion should be completely or partially gas-forming, and, finally, the conversion should be self-propagating.

Let us discuss somewhat in more detail the value of these conditions. The chemical conversion in the form of combustion or

detonation according to the very determination of these processes is self-propagating. Here in the latter case the self-propagation occurs with extremely high velocities. How is the ability of a chemical reaction toward self-propagation and its rate conditioned?

It is known that the rate of a chemical reaction (the number of molecules reacting per unit time in a unit of volume) depends on the concentration of the active particles. Inasmuch as this concentration increases with the temperature according to the known law $e^{-E/RT}$, where E - the energy of activation), then the rate of the reaction increases with temperature. The rate of reaction also increases with an increase in the concentration of the substance and, consequently, in the case of gases - with pressure, to which the concentration is proportional. With reactions of the first order, the rate of which is proportional to the first power of the concentration, the effect of the concentration is explained simply by the increase in the number of molecules in a unit of volume. With reactions of the second order, where the rate of reaction is proportional to the product or to the square of the concentration, the effect of the latter is explained by the fact that the number of collisions between molecules capable of reaction is proportional to the square of the pressure.

During the homogenous flow of the process the molecules entering into chemical reaction obtain the energy of activation with an exchange of energies with each other because of the fact that of the total storage of energy which is contained in the substance at the given temperature. This determines the dependence of the rate of reaction upon temperature.

In order to induce self-propagating conversion in the form of combustion, it is necessary to set fire to the charge of explosives at any place. Ignition means powerful and local initial heating; in the heated zone at a high rate (and respectively, high temperature) an exothermal chemical reaction occurs; the heat which is liberated with it is transferred to the neighboring layers of the explosives

and, in heating them, causes a rapid chemical reaction, which then is similarly induced in further layers. In the first place, the rate of the propagation of conversion under these conditions depends on its thermal effect, owing to which the heating of the substance occurs, and on the reaction rate of the reaction. In the second place, it depends on the conditions of the transmission of heat upon the zone of reaction into an unreacted substance, which determine the rate of propagation of the zone of high temperature.

Most rapidly the conversion would be extended in the case when the products of dissociation of one molecule were in a state directly to activate one or, all the more, several adjacent particles.

In the decomposition of typical explosives, for example, fulminating mercury or trotyl, 120-230 kcal/mole are liberated. The energy of activation of the slow caloric decomposition of these explosives is 30-40 kcal/mole. If the dissociation occurred at one stage, then each decomposed molecule could activate 4-6 others, and the dissociation of each of which would induce in turn the dissociation of the same number of adjacent molecules.

The dissociation of individual molecules occurs in any substance even at room, but the more so at increased temperatures. It, undoubtedly, occurs also under the effect of penetrating radiation, and in radioactive explosives, such as, radium azide, and under the action of intrinsic radiation. Nevertheless, a rapid accelerated decomposition of the explosives does not approach. It is not observed even during the action of fragments of the division of uranium, the energy of which exceeds by several orders the energy of activation of the explosives.

Thus, since the dissociation of an individual molecule of explosives does not lead to the rapid development of conversion, one should conclude that the second prerequisite of such a development, the dissociation of a molecule at one stage up to the products of complete conversion is not fulfilled. Actually, an experiment indicates that with all forms of conversion this dissociation occurs in

steps, and the thermal effect of the individual steps is much less than that of the complete thermal effect of conversion; apart from this, the energy of activation of some intermediate stages can be considerably more than the energy of activation of the initial stage or total process of dissociation of the explosives. Finally a chain development of the conversion cannot occur - the energy is liberated stepwise and is transferred to adjacent molecules by portions smaller than the energy of activation, being distributed in them in the form of heat. All this leads to the fact that the zone of maximum temperature located far from the surface of the explosives, the temperature gradient is small, and the rate of the propagation of heat, if it occurs by means of thermal conductivity, is also small.

One should add that this characteristic for explosives used in technology, is nonaccidental. The explosives, which would explode from the dissociation of an individual molecule or small number of them, are so dangerous during production and use that their use would be practically unreal. Therefore, the technical selection of a large number of chemical compounds able to explode is distinguished by those inducing the explosion of which is possible only by sufficiently intense pressure, the random formation of which was excluded. Strictly speaking, the discovery of contemporary - secondary explosives, which was accomplished about one hundred years ago, consisted in the fact that there were found explosives incapable of explosion from the action of flames, weak shocks, friction and other random actions possible in practice.

If the dissociation of an individual molecule of explosives does not lead to self-propagation of conversion, then the local dissociation of a considerable number of molecules, the formation of the origin of dissociation, can lead to it both with chain and thermal transmission of the reaction. In the presence of a chain reaction the number of abundant energies of particles of products of conversion arriving on one molecule in the layer of substance adjacent with the origin will be more. In the case of thermal acceleration of the reaction, the exothermicity of the conversion leads to the increase

in temperature, and, if dimensions of the origin are great, then with the propagation of heat into the surrounding substance a high temperature and, respectively, great rate of heat release will be maintained.

The examined scheme of the propagation of chemical conversion, in explaining combustion, does not include the propagation in the form of detonation; for this it must be taken into account that the rate of combustion also depends upon pressure. Furthermore, if combustion occurs on a surface considerably larger than the section of the charge, then the quantity of this section of explosives reacting on a unit of surface will be correspondingly more. Therefore, if there is created, simultaneously with the heating, high pressure and a developed surface of combustion, then the mass rate of propagation of conversion (in $\text{g/cm}^2\text{s}$) will have that order which is characteristic for detonation. It is obvious that the pressure during chemical conversion can arise only when its products at the attainable temperature are gases, if only partially.

Another characteristic of the detonation form of conversion consists in the nature of transmission of the energy: with the rapid passage of conversion there appears a sharp local increase in pressure, which is propagated in the form of a shock wave with supersonic velocity; this propagation leads to the excitation of chemical conversion in the form of combustion with parameters (pressure and a specific surface) characteristic for detonation.

The formation of a shock wave is also possible only if the conversion forms gases. Thus, the priming of pressure induced by the gases is not only one of two basic conditions of the rapid passage of the reactions of combustion (another condition is the high temperature), but also is the necessary factor of the rapid propagation of the process which is not carried out for the reactions, which do not form gases.

All forms of chemical conversion of explosives - slow thermal

conversion, combustion and detonation - are connected with each other both with respect to the nature processes proceeding with them and genetically. A slow chemical conversion can in defined conditions lead to the priming of combustion, and the combustion can turn into detonation; the transition of detonation into combustion is also possible.

Both the stationary processes of each of the three types and their mutual transitions are of considerable practical interest. During some processes of production of equipment and use are technological the possibility of heating of explosives to a relatively high temperature is desirable. At the same time such heating can lead to a firing of explosives or to considerable decomposition, which makes the explosives adequate for use. In order to prevent this possibility, it is necessary to know the conditions of the transition of the slow conversion into combustion.

A slow chemical conversion occurs even at the usual temperatures of storage of explosives, especially in a hot climate, determining their chemical stability. Apart from this, with prolonged storage of large masses of explosives a slow chemical conversion can lead even to spontaneous combustion. This conversion, is as a rule, a self-accelerating process, and if the storage lasts a very long time, and the mass of the explosives being stored is very great, then accumulation of heat is possible, which leads to spontaneous combustion. The task of the prevention of such a phenomenon is similar to the previous one, but often more complex, since it requires the knowledge of regularities of the dissociation at such low temperatures at which their direct termination by the usual method requires an extremely long time.

Characteristics of stationary combustion (the rate of combustion, the dependence of the rate of combustion and its thermal effect upon pressure, the dependence of the rate of combustion upon initial temperature) are of interest in all conditions of the technical use of a combustion, especially for a combustion in a semiclosed volume.

The transition of combustion into detonation is interesting in a number of aspects. In all explosives (except azide of lead) used in technology, the blast, friction and flame, if they are intense enough, initially cause the combustion, which can then turn into an explosion. The damage, created by the combustion of explosives, is the same character and scale as that with combustion (fire) without the participation of explosives. It is a different matter when the combustion is replaced by an explosion which causes great mechanical destructions both in its origin and at more or less considerable distances in the vicinity. One of the most important characteristics of contemporary secondary explosives substantially limiting their danger is the considerable stability of their combustion in its different possible conditions. The combustion of these explosives, induced by ignition or accidentally induced, for example, as a result of the burning and spontaneous combustion in production, with the exception of specific conditions which we will examine below, occurs without the combustion of detonation.

An even greater importance is the prevention of combustion from the transition into an explosion when using explosives for purposes of propelling. Capacitances in which there occurs combustion in missiles (the barrel of a firing weapon, the chamber of a rocket engine) are calculated for relatively small pressures, many times smaller than those which appear with detonation. The combustion of the latter means not only the failure of the shot, but also the bursting of the apparatus and frequently the death of its operating personnel.

Therefore, the necessary requirement for explosives used for throwing (powders) and for conditions of their use is the reliable stability of their combustion. Strictly, speaking, the most important stage in the development of powders in the past - the change from black powder to contemporary smokeless powders - to a considerable extent was dictated by the considerations of the stability of combustion. In the middle of the last century black powder began to satisfy the increased requirements with respect to the stability of combustion, and although with the disturbance of this stability the

process of combustion was not developed up to detonation, nevertheless the instability of normal combustion of black powder forced the failure of its application in favor of new powders - plastic types of powder on the basis of the high polymer - nitrocellulose. The physical features of these powder are thus distinguished from features of secondary explosives, which are their basic components, that combustion does not turn into an explosion even under those specific conditions at which this transition is possible in the case of secondary explosives.

The stability of the combustion of smokeless powder was so great that the question about it for a long time practically did not exist. It appeared again in connection with the new application of powders - for reaction propelling, at which disturbances of the stability of normal combustion are even more dangerous than that in barrel propelling. On the other hand, this type of throwing required the developments of new mixed powders, which with respect to its many features are intermediate between purely plastic powders and black powder. One of these features is the tendency increased in comparison with its predecessors, toward the disturbance of the normal mode of combustion, especially in new conditions of application. The elimination of this tendency, therefore, again acquired actuality.

In the example examined the instability of combustion is a serious deficiency. One hundred years ago this instability played a decisive positive role in the investigation of the method of activation of an explosion of new secondary explosives, and this method without substantial changes is important today.

Black powder is exploded from an ignition with a flame; secondary explosives, as is known, do not possess this ability, and in order to provide the possibility of their technical application, a simple and reliable method of activating their explosion was required. Such a method was found. Its basis was the main characteristic of the

priming explosives - the extreme instability of their combustion,¹ which conditions the ability to provide upon ignition a practically instantaneous transition of the combustion into an explosion. The small charge of the priming explosive, pressed into a metal case, with ignition at a distance by the same method which was used earlier for black powder or by another one, smoothly detonates and causes as much detonation as desired of the large charge of secondary explosives. From the given examples it is evident that the basis of those features which condition the methods of the contemporary technical application of explosives consists in characteristics of their combustion even, in the first place, the degree of its stability.

It was noted above that the phenomenon of the transition of detonation into combustion is possible. For condensed explosives this phenomenon is practically not studied. However, such a possibility caused in recent years a considerable interest in connection with explosive works in the coal mines, in which a methane or dust and air explosive mixture can be formed. During the explosion of a charge of explosives in a fuse in those conditions in which this explosion by itself is safe with respect to the combustion of the ignitable air, the stopping of detonation and combustion instead of it the priming sharply increases the danger of the indicated combustion. In this plan the possibility of the stopping of detonation of a charge of explosives and the subsequent priming of combustion of the residue of the charge attracts the attention of many investigators, who see in it the basic source of the danger of explosive works in reference to the priming of an explosion of methane or dust and air mixtures.

¹It is understandable that the subdivision of explosives into secondary, priming and projectile explosives according to the criterion of the stability of combustion is to a certain extent conditional, inasmuch as this stability depends not only upon the chemical identity of explosives, but also upon the physical structure of the charge, but also upon the conditions of combustion; with the change in these factors it is possible to change substantially the degree of stability of the combustion of the majority of explosives.

CHAPTER III

STABLE COMBUSTION OF EXPLOSIVES

I. Method of Investigation

1. Manometric Bomb

The basic, and until recently, practically sole laboratory instrument for the determination of pressure during combustion, the quantity and the composition of the gases, and also the dependence of the rate of a combustion upon pressure was the manometric bomb of Sarro and Vieille [111]. This instrument allowed studying the combustion of powders at pressures up to several thousands of atmospheres, at which they are used in barrel firearms. Manometric bomb in its time made it possible to establish some fundamental regularities of the combustion of black powder, which were the theoretical basis for the development of contemporary powders of the colloidal type, the ballistic investigation of which until now basically has been conducted in a manometric bomb.

The manometric bomb, schematically shown on Fig. 76, is a heavy-walled durable steel tube 2 with an interior volume of 22 cm³ and above, into which from both sides plug 1 and 4 are screwed.

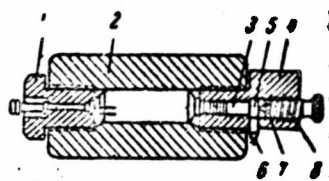


Fig. 76. Diagram of the layout of a manometric bomb.

Plug 1 has a central electrically insulated rod and is for igniting the gunpowder charge with the help of an igniter, ignited in turn by a filament of a fine wire by an electrical current. Plug 4 has a central channel, in which a well-fitted piston 3 moves. Between the head of this piston 5 and plug 8, screwed into plug 4, there is placed a pressure meter, in the capacity of which a copper crusher gage 7 of definite dimensions was used and is widely used today and the compression of it characterizes the magnitude of the pressure. In order to obtain the characteristic of the change in pressure with time, the movement of the piston is written usually by a steel pen 6 directly fastened to its head on smoked paper stretched over a rotating drum. This recording gives the change in pressure from the moment of the beginning of pressing of the small copper cylinder to the moment of the achievement of maximum pressure - a decrease in pressure with the use of a small copper cylinder, naturally, cannot be recorded. The conversion of the pressing of the small copper cylinder into units of pressure is produced taking into account the cross section of the piston on the basis of experiments of the pressing of a series of small cylinders on presses at definite static pressures.

The determination of pressure during combustion in the bomb is complicated by a number of factors. Thus, the pressing of the small copper cylinder depends not only upon the magnitude of the pressure, but also on the rate from which this pressure has been achieved. With the instantaneous increase in pressure pressing is obtained because of the inertia of the piston two times more than with static or slow pressing. The calculation of pressure in the cases intermediate between these maxima is complex. Inasmuch as the magnitude of pressing depend on the mass of the piston, then, by changing the latter, it is possible to approach one of the extreme cases.

Further, by using usual cylindrical copper crushers, it is not possible to record in detail the change in pressure in the field of small pressures. This deficiency is eliminated by the application of small copper cylinders curved to a cone, proposed and introduced into the application by Serebryakov [112]. Finally, the application of

irreversibly deformed metal cylinders as sensors allows the recording of only the increase in pressure but not its drop.

A series of instruments with small inertia has been developed for the recording of pressures rapidly changing both on the side of an increase and on the side of a decrease [113]. In the majority of them used as a sensing element is a circular diaphragm or plate, rigidly fixed on the periphery. The sag of the diaphragm can be determined by various methods - by the application of an optical indicator, optical interference, electrical condenser, alternating magnetic resistance, the resistance strain gage. A piezoelectric sensor is especially suitable for the measurement of very rapidly changing pressures; a charge appearing with the application of force is recorded after amplification by a loop or cathode-ray oscillograph.

The factor which distorts the result of the measurement in a manometric bomb is the cooling of the gases of combustion as a result of heat emission to walls of the bomb. It is true that at great average pressures, i.e., at short times of combustion, heat emission is comparatively small and can be taken into account approximately; however, at low average pressures its effect is considerable.

By experiments in a manometric bomb, in principle, it is possible to determine also the rate of combustion and its dependence on pressure. However, such a determination is considerably less reliable than the measurement of pressure.

An experiment in a bomb allows judging only indirectly the magnitude of the rate of combustion - from the magnitude of the pressure of gas products of combustion, proposing a definite dependence between this pressure and the quantity of the substance burned up.

This judgement, however, is entirely reliable only with the fulfillment of a number of prerequisites.

1. If combustion occurs instantly and simultaneously over the entire surface of the charge. This condition is impracticable.

Especially at low pressures developed by the ignition charge, a relatively great delay of a combustion and also the nonsimultaneous action of it takes place. At high pressures of the igniter the initial section of the pressure curve reflects the isochronous combustion of both the charge and the igniter.

2. If the composition of gas products of combustion and their temperature are invariable at all pressures. This condition is not fulfilled both at low pressures, when the composition of the gases does not correspond to the equilibrium (nitrogen is obtained in this case mainly in the form of NO), and at increased pressures, when the equilibrium between the individual components of the products of combustion can shift depending on pressure.

3. If the so-called geometric law of combustion is fulfilled, i.e., if the combustion occurs over the entire surface perpendicular to it and at a constant rate. This law is also **not** fulfilled especially when during combustion the gases move along the burning surface at considerable velocity.

4. If the dependence of the rate of combustion upon pressure in the whole examined interval is the same. An experiment shows that for the wide intervals of pressure this condition is also not fulfilled.

Furthermore, inasmuch as the process occurs not at constant but at increasing pressure, the combustion of a creation (heated) layer in the beginning of combustion can occur depending on the conditions of the combustion with a greater rate than that which corresponds to stationary combustion at the given pressure. Further, inasmuch as the pressure during combustion increases, the thickness of the heated layer is changed, which is also reflected in principle on the magnitude of the rate of combustion. Finally, combustion at the end for the same reason is unavoidably nonstationary.

All these circumstances affect the rate of combustion and in a greater degree, the less the depth of the powder cells. The described

factors obtain an especially great importance during research on combustion under moderate pressure. Vieille himself, in describing his method, notes the imperfection of information on combustion obtained from experiments in a manometric bomb and also the lack of the methods of the direct determination of the rate of combustion of high pressures.

2. Instruments of Constant Pressure

Taking into account considerations examined above, it would be expedient to develop methods of the investigation of combustion at constant pressure especially as in a reaction firearms replacing the barrel firearms, the usual mode is namely combustion at constant pressure. It is methodical, however, to study the process in these conditions more complexly, since it is not possible to use, as in a manometric bomb, the change in pressure as a criterion of the course of combustion; in this case it was necessary to provide the possibility of conducting experiments at various temperatures; the possibility of a direct observation of the process also was desirable.

The rate of combustion at constant pressure can be determined by carrying out the combustion of a charge in a chamber with a nozzle. If the surface of a charge is constant, then the pressure for the extent of combustion barely changes. In this case the linear rate of combustion can be calculated as the ratio of the half-thickness of the wall (depth of the arch) of powder tube to the time of combustion. The advantage of the method of determination is the closeness of conditions of combustion to conditions of the real application, and the deficiency - the necessity to prepare comparatively large specimens of powder. Furthermore, in the experiment it is difficult to exclude the effect of some secondary factors (nonsimultaneous state of the combustion of the charge over entire surface, the rise in pressure conditioned by the combustion of the igniter, the motion of gases along the burning surface and others). Simpler in laboratory fulfillment and not requiring the large quantities of powder is the determination of the rate of combustion at constant pressure of the

cylindrical charge armored on the lateral surface, being ignited on the end with the recording of the time of combustion of the section of definite length or movement of the zone of combustion with time.

The first instrument, developed for these purposes by Varga [114], was a glass tube with a diameter of about 30 mm and sealed underneath. In the upper part the tube has two side branch pipes. One of them connects the tube with the pressure indicator, and the other - with a vessel of great volume into which during combustion enter gases, owing to which in a tube practically constant pressure is maintained. Above the tube is closed by a rubber plug through which passes a thin (sealed below), small glass tube for a thermoelectric couple and a second small tube for the conductors of a current, which is finished by an ignition spiral of thin wire. Fastened to this second small tube is a column of powder or explosives usually so that it does not touch its side surface of the tube holder in order to avoid additional heat losses because of heat emission to the tube holder.

If the examined substance is a liquid or powdery, then it is placed into the small glass tube of small diameter; if the substance is able to retain its form, then it is used in the form of the cylindrical charge, shielded on the side surface by any incombustible or barely combustible insulation in order to prevent the transition of the combustion from the end to the side surface; this is especially important in the combustion in the atmosphere of air.

The temperature explosives can be regulated by submerging the tube at sufficient length of it in a thermostat of the usual type or into a Dewar flash.

The pressure at which the experiment should be conducted is established, either by pumping out the air partially from the system or by admitting into it air, or better yet, an inert gas.

The deficiency of this version of the instrument is the fact that the rubber plug covering the tube is not held in it at a pressure

of 2-2.5 at. At the same time the glass tube itself withstands considerably greater pressure and is broken only at 70-80 at. For these reasons another version was accepted (Fig. 77). A metal tube with the internal diameter somewhat exceeding the external diameter of the glass tube was connected with it with the help of Mendeleyev cements. Above metal tube was closed by a cap screwed on with an insulated rod passing through it to which a column of the tested explosives was fastened. The metal tube had two side branches - for connecting with a pressure indicator and with a vessel. In such a system a great number of experiments was carried out at pressures of about 20 at, and, the ruptures of the glass tube were an infrequent phenomenon, especially when an intermediate glass tube for the moderation of the heating by gaseous products of combustion of the external glass tube is used.

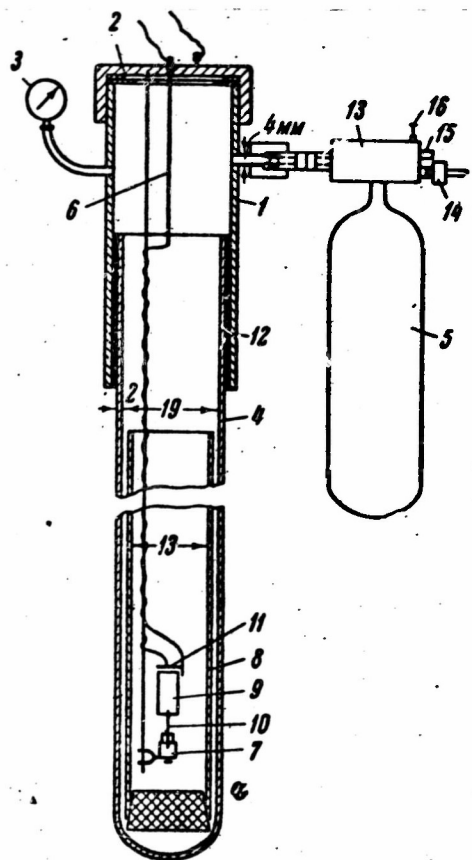


Fig. 77. Diagram of an instrument for the study of combustion at moderately increased pressures. 1 - steel tube; 2 - screwed cap; 3 - pressure indicator; 4 - glass tube; 5 - vessel; 6 - rod electrical conductors; 7 - charge holder; 8 - internal glass tube; 9 - powder charge; 10 - needle; 11 - spiral for combustion; 12 - Mendeleyev cement; 13 - distributive box; 14 and 15 - valves for connection with the vacuum pump and gas cylinder; 16 - branch pipe for connecting the system with the atmosphere.

With slowly burning substances the time of combustion can be measured by a timer. With short times of combustion, and if it does not form opaque products, the total time of light emission is determined by photographing the burning column from the end. With the transparent shell of the column it is possible to photograph the movement of the glowing front of the combustion. In both cases the photographing is produced on photographic film moving at a definite rate. The second method is more preferable, since it makes it possible not only to establish the general time of the combustion but also quantitatively to indicate the change with time of the rate of combustion, if such takes place.

In certain cases, if the light emission of the combustion front is too weak or opaque products are formed, the photographing of light emission cannot give a clear picture of the propagation of combustion. It is possible to decrease the absorption of light emission by the opaque products of combustion if we place between the charge and walls of the clear tube a clear prism with plane-parallel walls, which prevents the entrance of opaque products into the space between the column of explosives and the objective of the camera. In such cases the shadow method of the photographing of combustion is applicable [115] (Fig. 78). The column of explosives is illuminated by a narrow intensive band of light of source 1, and on the moving photographic film the image of this band is recorded, and its width increases according to the combustion of the column and to the decrease in altitude of the shadow formed by it (see the photo for the potassium picrate, Fig. 79). The photographing of the movement of the front of the combustion in the reflected light is still more expedient but more complex in fulfillment and therefore was little used.

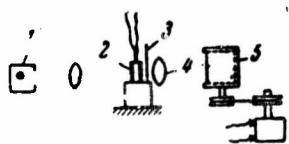


Fig. 78. Diagram of a device for a shadow photographic method of the determination of the rate of combustion. 1 - source of light; 2 - small cylinder; 3 - slit; 4 - objective; 5 - cylinder with film.



Fig. 79. Photograph of the combustion of potassium picrate.

With all these versions frame filming of the burning column with a definite interval between the frames is applicable also. The decrement in height of a column allows calculating the rate of combustion. Finally, the recording of the time of combustion is possible with the help of two thin wires of an appropriate metal passing through the column of the explosive at a definite distance from each other and being fused upon combustion [116]. The moments of breaking of the wires are recorded with respect to the stopping of the current passing through each of them by any of the many methods existing for this purpose. This method gives, naturally, only the average rate of combustion; furthermore, during rapid combustion, especially when the temperature on the surface of separation of the condensed phase and the initial products of combustion is low, the apparent and nonuniform delay of the melting of the wire is not excluded. The advantage of the method, especially important if experiment is conducted with increased or reduced temperatures, is the possibility of working in an opaque vessel.

Inasmuch as, however, in most cases the photographic method of recording of the propagation of combustion deserves preferences, then together with the instrument in which combustion occurs in a glass tube, i.e., at pressures not exceeding several tens of atmospheres there was developed a number of the designs of a bomb of constant pressure in the form of a steel container equipped by one or several small windows of plastic or inorganic glass. The bomb has a rather large volume or is connected with a vessel of sufficient dimensions in order that the increase in pressure in experiments would not exceed the given magnitude; correspondingly the section of the tube which

connects the bomb with the vessel is also selected. The first of the Soviet models of the bomb was designed by Bakeyev [117].

The bomb, engineered at the Institute of Chemical Physics of the Academy of Sciences of the USSR, is a thick-walled steel glass with an internal diameter of 10 cm and volume of 1 l, the strength of which allows the leading of experiment at pressures up to 150 at. In the cylindrical part the bomb there are two plexiglass windows, located opposite each other. From above the bomb is closed hermetically by means of a rubber gasket by a steel cover (Fig. 80), which has 10 openings by which the cover is put onto bolts fixed in the housing of the bomb; the bolts have threads on which are screwed nuts, which press the cover to the end of the bomb. Mounted on the cover of the bomb are several electrical leads, used for igniting the charge, measuring the temperature, etc. On it there is also a valve which is connected to the pressure indicator and serves for the filling of the bomb with gas and the outflow of the gases of combustion after an experiment. Fastened on the lower side of the cover are two rods; joined to them is the support, in the center of which is installed the specimen of explosives. An igniting spiral is fastened to a spring located in the upper part of the bomb, and with the help of a filament it is pulled to the end of the charge. With the combustion of the explosive the filament burns, and the spiral is removed by the spring from the burning surface. If this is not done the spiral can be greatly incandesced as a result of the catalytic burning out on it of intermediate products, and this can affect the process of combustion and especially the composition of its products.

A bomb of constant pressure of another design [118], which allows the conducting of experiments at pressures up to 350 at, is shown on Fig. 81. The housing of the bomb is a thick-walled steel container with a capacity of 3 l with windows of plastic. Through one of the windows the process of a combustion is recorded; the remaining windows serve for lighting in taking pictures of combustion or for focusing the photorecorder. Mounted on the cover of the bomb is a stand. Fixed in the cover are current carrying plugs, which are insulated from the housing of the bomb. The cylindrical charge of the

tested explosives in a small clear tube is placed in a special holder (Fig. 82), installed in the center of a stand. The holder has thin horizontal strips lying against the middle part of the charge, the distance between which it is possible to measure accurately. These strips give a shadow on a photograph and allow determining the height of that part of the charge which is located between them.

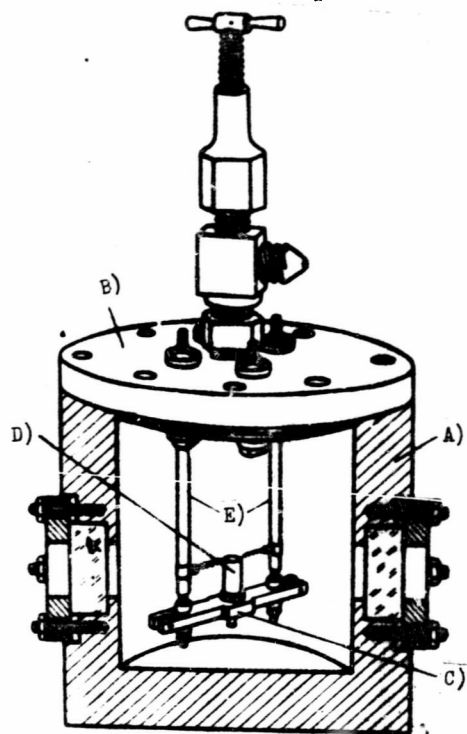


Fig. 80.

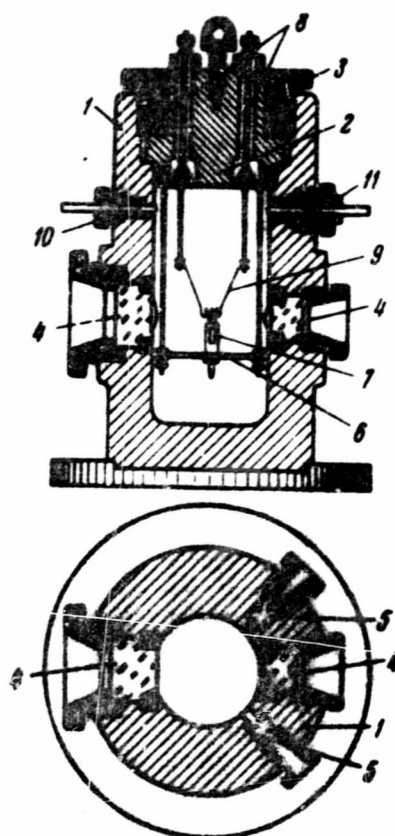


Fig. 81.

Fig. 80. Diagram of a bomb with devices for the ignition of powder. A) housing of the bomb; B) cover of the bomb; C) support for the tested specimen; D) explosive specimen; E) insulated electrical leads.

Fig. 81. Diagram of a bomb of constant pressure up to 350 at. 1 - housing; 2 - cover with sealing ring; 3 - pressing ring; 4 - window for recording the process of combustion; 5 - window for lighting; 6 - stand for the specimen; 7 - explosive charge; 8 - insulated electrical leads; 9 - spiral of Nichrome wire for combustion; 10 and 11 - inputs for connection with the compressor and valve for discarding the gas from the bomb after an experiment.

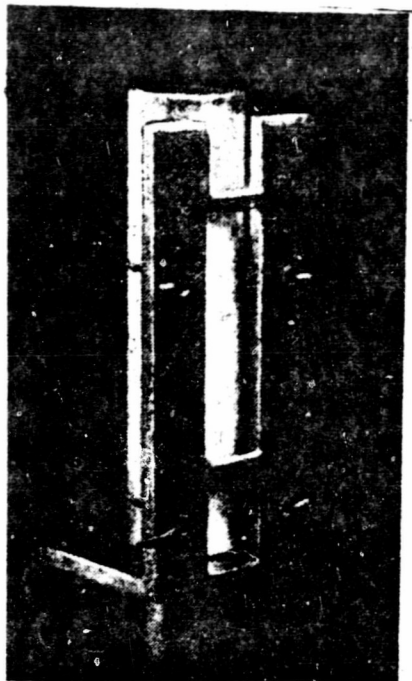


Fig. 82. Templet for a tested specimen.

For experiments at increased temperatures in the bomb a thermostat can be installed. This thermostat (Fig. 83) is a massive cylinder of red copper heated by the current and is well thermally insulated. The temperature of the cylinder is measured and controlled by two thermoelectric couples; it is maintained constant with the help of an automatic electronic regulator with a recording device. The thermostat has a deep channel along the axis for placing charge and two narrow recesses, which with the closed cover of the bomb are located against its window. The recesses are closely closed by glasses for the decrease in the heat exchange because of convection. The height of the thermostat and also the arrangement of heating elements provide practically constant temperature of the charge over its entire length.

Determination of the rate of combustion at a constant pressure was produced and at considerably higher pressures - up to 10,000 at [119].

One should show that the distinction between the bomb of increasing pressure and the bomb of constant pressure is referred more to the method of the operation than to the layout of the bomb. In

essence this distinction consists in the magnitude of the density of charging at which the experiment is produced. If it is great, then the pressure increases and this increase can be used for measuring the combustion, according to which the rate of combustion can be calculated. The average rate of combustion was thus determined in the experiments of A. P. Glazkova on the combustion of ammonium nitrate and of its mixtures with various catalytic agents. A similar method was used by Belyayev and collaborators [120], who measured the average rate of combustion of some explosives, using combined charges from successively located columns of different substances. The recording pressure-time curve had in this case the form of a staircase (Fig. 84), according to the width of the steps of which it is possible to determine the time of the combustion of each column at a certain average pressure, which corresponds approximately to the middle of the height of the step. H. A. Kornin, in changing the surface of cooling in the manometric bomb in accordance with the rate of heat release, carried out combustion in it at practically constant pressure; however, in this case it is necessary to provide the recording of the moment of termination of combustion, which is connected with known difficulties.

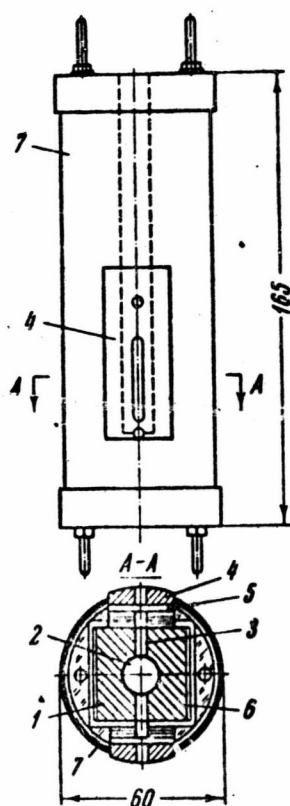


Fig. 83. Diagram of a thermostat for the conducting of experiments at constant pressures and increased temperatures. 1 - block of red copper; 2 - the cylindrical channel into which the carrier with a charge is placed; 3 - slot-like recess; 4 - frame; 5 - glass; 6 - heating winding with insulation; 7 - case.

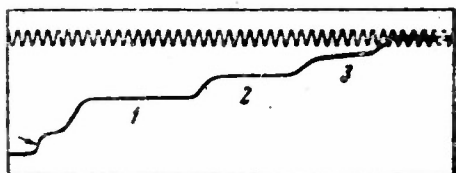


Fig. 84. Curve $p(\tau)$ during the combustion of a combined charge, which includes three small cylinders of trotyl (1, 2, 3) of known length and four small cylinders of an auxiliary substance with a large value of $dp/d\tau$.

In the investigation of combustion under low pressures the determination of volume and composition of the gases being formed is sometimes necessary. For this purpose Sarrau and Vieille [121] used the following method. The explosive was placed into the small glass tube ($d = 4$ mm) connected with the rubber vessel into which during combustion the formed gases entered. Before the experiment the connecting glass tube was filled with carbonic acid, the volume of which was taken into account with subsequent analysis of the gases.

In many works the determination of the volume of gases was produced in the following manner. A charge of explosive was placed into a round-bottom flask, which was filled with inert gas for the prevention of the possible participation of air in the reaction of combustion and the subsequent interaction of oxygen with the nitric oxide. Before the experiment in the flask evacuation was created with such a calculation that the average pressure during combustion would correspond to that desired. The explosive was ignited by a spiral. After the cooling of gases of combustion down to the temperature of the ambient air their pressure was measured, and according to standard equations the volume of gases was calculated.

For the determination of the composition gases were collected in the instrument shown in Fig. 85. Placed into the lower part of the glass tube 1 with a diameter of about 15 mm was a small tube 2 of explosives. Tube 1 is united by a T-joint 5 with a vessel 3 filled with mercury and connecting rubber tube with a level vial 4. With the firing of the explosives gases emerge into the air, washing the system of it. After a certain quantity of explosives burns, the elbow 6 of the T-joint is closed, and gases enter into the vessel with simultaneous lowering of the level vial. A deficiency of the method is the fact that it is difficult to use for the collection of gases during

combustion under increased constant pressures. Another version of the scheme of the instrument used for this purpose is described in work [122].

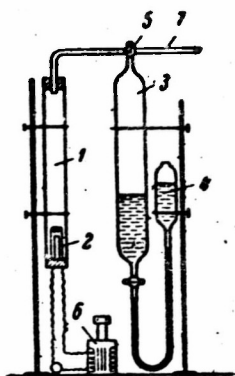


Fig. 85. An instrument for the collection of gaseous products of combustion.

For the determination of the composition and quantity of the gaseous products of combustion, in the first place the relationships between their individual components, it is possible to use the bomb of constant pressure, especially if the inert gas which is used for the generation of pressure is different than those gases which are formed during combustion.

The determination of the composition of gases is usually produced with some additions by the method which has a wide application for the analysis of furnace gases. Gases successively pass through the absorption vials with the appropriate agents: 1) for the absorption of carbonic acid a concentrated (60%) solution of caustic potash; 2) for the absorption of nitric oxides a solution of iron sulphate (oxide) acidified by sulphuric acid; 3) for the absorption of oxygen an alkaline solution of pyrogallol; 4) for the absorption of carbon monoxide an ammonium solution of cuprous chloride. After the absorption of vapors of ammonia residual gases are mixed with oxygen or air and proceed to burn over platinum spiral. The quantity of methane was determined according to the quantity of carbonic acid formed and the quantity of hydrogen - according to the decrease in volume. After the burning again the quantity of oxygen was determined in order to be convinced of the absence of the nitrogen oxide and also the other

hydrocarbon besides methane. The nitrogen was calculated according to the difference.

The nitrogen dioxide formed is usually very small, and it is not determined; when necessary the nitrogen dioxide can be determined colorimetrically or by some other method in fluid of the first vial, which absorbs NO_2 together with carbonic acid.

The most reliable method of the determination of nitrogen oxide, inasmuch as the elasticity of its vapors at low temperatures greatly differs from the elasticity of the vapors of nitrogen oxides, elementary nitrogen and CO, is fractional freezing. After the isolation of N_2O from other gases, it is possible to produce its burning in an atmosphere of hydrogen or absorption in ethyl alcohol.

II. Maximum Conditions of Combustion

The simplest case of combustion is its one-dimensional propagation in an extended, for example, cylindrical charge ignited on the end. An experiment shows that combustion is possible only if the diameter of the charge exceeds a certain magnitude - critical diameter.

The critical diameter is usually defined as the diameter extinguishment of the combustion of the slightly narrowing charge ignited on the wide end. It is possible to conduct an experiment in telescopic tubes with transient sections in the form of a truncated cone. The critical diameter can be determined also by successive experiments with cylindrical charges of various diameters widened at the ignited end. With the conducting of experiments at various pressures it is expedient to place the charges in a fluid (for example, in water) in order to provide the constancy of the temperature coefficient of thermal conductivity of the surrounding medium.

The critical diameter depends not only upon the nature of the substance, but also upon the conditions of combustion, in the first place, upon pressure and initial temperature and for powdery explosives

also on cubic density. Table 13 gives the rates of combustion of a number of explosives at low pressures and critical conditions of combustion for those explosives for which they were determined.

Table 13. Values of rates and of critical diameters of combustion* for a number of explosives at atmospheric pressure (in air).

Substance	Density, g/cm ³	Critical diameter of combustion, mm	Rate of combustion, cm/s	Remarks
Trotyl.....	1.5	~30	-	
Tetryl.....	1.0	9	0.067	
Hexsogen.....	0.9	~2	0.042	
PETN.....	1.2	30	0.023	At somewhat increased pressures PETN at this diameter did not burn
Dyne.....	1.5	9.5	0.051	
Powder N.....	1.5	9.3; 11.2	0.060	-
Nitroglycerine.....	1.6	0.5	0.14	-
Nitroglycol.....	1.5	1.0	0.030	-
Diglycoldinitrate.....	1.39	5	0.012	-
Ammonium perchlorate..	1.0	33	-	The given value of the critical diameter refers to the finely dispersed product of factory manufacture; the pure perchlorate ground in motor did not burn even with the diameter of the charge at 40 mm

*When the graph for the critical diameter two numbers are given, the smaller of them denotes the greatest diameter of the cylindrical charge at which burning is not propagated and the larger number - the least diameter at which it is propagated. If one number is given, it denotes the diameter of extinguishment of the conical charge.

The existence of critical conditions of combustion is conditioned by the following reasons. The propagation of combustion occurs because of the transfer of the heat liberated by the exothermal reactions which occur in the reactive layer adjacent to the layer of explosives. This heat heats the layer of the explosives, which enters into reaction up to such a temperature beginning with which the rate of exothermal reaction is sufficiently great in order that the heat arrival would compensate the heat losses and the rate of reaction would increase independently. However, heat losses from the heated layer take place both for the heating of the next layer of the explosives and into the environment. If the temperature to which there

is heated the layer entering the reaction is inadequate, then the rate of the reaction and, respectively, the heat arrival is less, and the latter cannot compensate the heat removal. Then the temperature of the layer cannot increase because of the reaction developed as a result of the self-heating up to the maximum temperature of combustion, and, in passing through a certain smaller maximum, it falls. The next bed obtains even less heat, the maximum of temperature in it proves to be even lower and so on. Thus, as a result of heat losses combustion rapidly ceases.

All factors which impede heat removal into the environment, and also, as a rule, into the depth of the explosives they favor combustion. In exactly the same manner those factors which increase the rate of the chemical reactions releasing heat facilitate combustion.

In light of these considerations the effect on the possibility of combustion of the diameter of the charge, the rate of combustion, pressure, initial temperature and cubic density, and also characteristics of its shell becomes understandable.

The effect of the diameter and other parameters on the possibility of combustion is explained in principle in the same way as their effect on the thermal spontaneous ignition which appears with uniform heating of the explosives. In the latter case the heat arrival is proportional to the cube of the diameter and the heat removal with convective heat exchange - to its square; with conductive heat removal its magnitude increases with the diameter more slowly; into the Frank-Kamenetskiy criterion the diameter enters in the second degree - with an increase in diameter the path of the heat increases from the place of its release up to the wall.

The reason for the existence of the critical diameter of combustion are similar in principle also to those which determine the existence of the critical diameter of detonation. The possibility of the propagation of the latter is conditioned by the relationship of

the rate of the liberation of energy and the rate of its removal into the environment. This relationship determines the magnitude of attainable pressure upon which the rate of detonation conversion depends. Furthermore, the quantity of separable energy is proportional to the volume of the charge, and the quantity of energy lost into the environment depends on the relative surface of the charge. A basic distinction consists in the fact that with detonation the rate of the conversion completely greatly increases with an increase in pressure and is respectively decreased by "losses" (drop) in pressure. Heat removal because of the high rate of the process does not play a real role. In this sense the concept of the critical diameter of detonation is more complex; it appeared in the science of explosives later (1940) than the concept of critical diameter of combustion (1934). It is natural that the critical diameter of detonation, unlike the critical diameter of combustion, does not depend on external pressure - pressure attainable with detonation conversion several orders higher than those pressures which can be realized during an experiment.

In light of role of the diameter as a factor determining the magnitude of heat losses, it is natural that the less the magnitude of the critical diameter, generally speaking, the higher the rate of combustion. At the greater rate of combustion the portion of heat released to the environment is less (other conditions being equal).

Beside the magnitude of the rate of the combustion, it is necessary, however, to take account of the nature of the combustion. If the subject under discussion is about a volatile substance like nitroglycol, whose condensed phase is heated only up to the boiling point, then the losses of heat because of thermal conductivity of the fluid are small, and the critical diameter is small (1 mm) despite the small rate of combustion (0.03 cm/s). If combustion is accompanied by considerable heating of the condensed phase, just as during the combustion of smokeless powder, then because of great thermal losses the critical diameter is much more despite the high rate of combustion.

The great critical diameter of combustion is conditioned in this case by losses of heat, and this can be shown in the example of nitroglycerine powder, which in an asbestos winding burns only with a diameter of not less than 20 mm, and being ground into powder, and besides relatively coarse powder, it burns in a glass tube even with a diameter two times smaller. For the same reason pyroxylin burns in glass tubes with a diameter of about 5 mm, but pyroxylin powder even with a very small content of volatile substances does not burn with considerably greater diameters.

The effect of pressure on the possibility of combustion is explained in the following manner.

The increase in pressure, increasing the rate of combustion, decreases the comparative heat losses and, respectively, critical diameter. Similarly the initial temperature affects, and its increase increases the rate of combustion and, furthermore, decreases the drop in the temperature between the explosive and the environment; for these reasons the comparative heat losses during combustion decrease.

For powdery explosives the magnitude of the critical diameter depends also upon cubic density. The increase in cubic density can both facilitate the combustion, i.e.; decreases the critical diameter (fusible explosives, for example, tetryl), and to impede it, i.e., increase the critical diameter (infusible explosives, for example, nitrocellulose). At first sight the opposition of the effect of density in both cases is paradoxical. We will see, however, below (page 177) that in this case it can be explained by simple considerations relative to the effect of density on heat removal.

The possibility of combustion is also affected by the shell of the charge - the thermal conductivity of its material and thickness of the walls. For materials with considerable thermal conductivity (glass, metals, etc.), at greater thickness of the wall of the tube the minimum diameter is more. This is explained by the fact that with combustion in air the magnitude of heat losses is determined basically

by the coefficients of the transition of heat from explosives and products of combustion to the tube, by thermal conductivity and by the thickness of its walls. Heat emission from the tube to the air is relatively insignificant just as thermal conductivity and the heat capacity of the air.

The effect of the thickness of the wall can be illustrated simplest by the following experiment. A narrow small tube with nitroglycol or hexogen is submerged by its lower half into water. Combustion, which normally is propagated in the upper part of the small tube, ceases, reaching the level which corresponds to the level of the water outside the small tube. If we take a substance, which burns more rapidly, for example, methyl nitrate, then the water does not manage to take part in the heat exchange, and combustion does not attenuate but continues, and the rate of it only insignificantly is less than the rate of the combustion of the upper section.

In more detail the effect of the thickness of the wall was studied in the example of the combustion of hexogen in gypseous tubes (Table 14). It was established that at too large a thickness of the wall of the tube (its internal diameter was constant - 7.8 mm) combustion attenuates. If the thickness of the wall is less than 4 mm, it is propagated to the end of the charge. Here, in the case of a thicker wall, the rate of combustion is somewhat less. If the substance is heated preliminarily, then combustion is possible with a greater thickness of the wall.

Table 14. Effect of the thickness of the wall of a gypseous tube on the combustion of hexogen.

Thickness of wall, mm	1.8	2.2	4.0	3.9	5.7	5.9	9.9	10.3	20.8	20.8	5.8	10.3	20.8
Linear rate of combustion, cm/s	0.066	0.067	0.055	Combustion was extinguished							0.052	Combustion was extinguished	

Note: The cubic density fluctuated within limits of 0.97-1.04 g/cm³, the temperature of the substance in the first ten experiments was +20.5°C, and in the last three experiments it was +85°C; the external pressure was 748 mm, and the interior diameter of the tube in all the experiments was 7.8 mm.

Trotyl behaves similarly. In glass tubes combustion is propagated with a diameter of 27 mm and above; the covering of the tube with asbestos cord somewhat increases the rate of combustion.

In bronze tubes with a diameter of 30 mm with a thickness of the wall at 1, 5, 8 and 10 mm combustion is not propagated. If in a tube with the thickness of the wall of 1 mm we decrease the heat removal into the air, having wound it with asbestos cord, then combustion becomes possible, and its rate (0.015 cm/s) is noticeably more than that in glass tubes (0.011 cm/s). In this case the combustion toward the end is accelerated and becomes nonuniform, obviously, as a result of the heating of the explosive in the lower part of the tube because of the transfer of heat along its walls. In thicker walled (5, 8 and 10 mm) bronze tubes combustion is not propagated also with the covering by asbestos cord.

Given considerations and examples explain mainly the impeding effect of the shell of the charge on combustion. The shell, however, can also have a reverse effect. With not too large a relative thickness of walls of the shell, great thermal conductivity of its material and low rate of combustion, the heat from products of combustion can be transferred to the explosive along the walls of the tube faster than through the front of the combustion, and this effect can prevail over the effect of losses of heat on the heating of the walls and the medium surrounding the tube. This effect appears most visually if into a glass tube with a slowly burning explosive - nitroglycol - one inserts a rod of small diameter consisting of metal with great thermal conductivity (red copper), and the rate of combustion of the liquid in this case greatly increases. It is obvious that the reason for this increase in the rate of combustion is the supplementary heat feed to the liquid about the copper rod. The same role - the supplementary heat feed - can be played by thin walls of the tube in which there occurs combustion, if they are made from a material of great thermal conductivity. Actually, in thin-walled metal tubes the rate of combustion proves to be higher than that, for example, in glass tubes. Thus, fulminating gelatin in brass tubes ($d = 28$ mm, $s = 1$ mm,

l = 5) burned with an average rate of 0.195 cm/s, while in glass tubes the rate of combustion was only 0.142 cm/s. Moreover, in brass tubes the rate of combustion had an accelerating nature - the average rate with the length of the tube of 24 cm increased up to 0.340 cm/s.

In experiments with fulminating mercury, pressed up to great density into a reddish copper case of a priming cap-detonator, there was observed the transition of combustion into detonation, which did not occur, if the explosive was pressed directly into a thick-walled steel die. The apparent reason for the initiation of detonation, in the first case, was the heating of the thermal wave, which is rapidly propagated along walls of the case.

For PETN, which burns relatively slowly, the acceleration of combustion as a result of the propagation of heat in walls of the tube was observed even in glass tubes: in tubes of smaller diameter combustion was faster [123].

If the combustion of nitroglycol is conducted in one of the elbows of the connecting glass vessels, maintaining the level of the burning liquid constant, then because of the intensified heat feed on the walls the rate of a combustion greatly increases.

The same was observed by Adams and Stokes [124] in the combustion of hydrazines. The 97.7% hydrazine burned at atmospheric pressure in nitrogen (diameter of the tube, 3 mm) at the rate of 0.031, and with a diameter of 5 and 10 mm - at the rate of 0.027 cm/s. Authors connect this effect of the diameter of the tube with the dependence of the area of the surface of the gas-phase flame, which was relatively more in narrow tubes. With this explanation it is possible to agree, to be more precise, that the increase in the relative surface of the flame is not the reason for the increase in the rate of combustion, but a consequence of the fact that because of the intensification of the heat feed along the walls of the rate of steam generation increases. In order that a greater quantity of the vapors would be able to burn, naturally, the surface of the flame should become more, similar to the way it occurs in a Bunsen burner with the increase in the rate of the admission of gas.

the way it occurs in a Bunsen burner with the increase in the rate of the admission of gas.

It is understandable that the described effects can take place only at a small rate of combustion, when the rate of propagation of a thermal wave over the material of the shell is commensurable with the rate of combustion. Therefore, for example, with an increase in pressure, which increases the rate of combustion, but does not change the thermal conductivity of the shell, the accelerating effect of the latter will decrease. The same refers to the negative effect of the shell on the possibility of combustion.

The effect of pressure on the critical diameter of combustion of nitroglycol was studied by A. F. Gushchina. At pressures of 0.57, 1.0 and 2.0 at combustion in conical tubes extinguished with the achievement of a diameter of 1.7, 1.0 and 0.5 mm, respectively. It is interesting that the product of pressure by critical diameter is a constant magnitude. V. E. Annikov determined the critical diameter of combustion of cast trotyl in an interval of 10-350 at. An explosive was located in the narrowing glass tubes submerged in the basic part into water at 10°C and was ignited from the wide end of the tube in a bomb of constant pressure. As is evident from Fig. 86, the critical diameter of combustion at 10 at is ~ 10.5 mm and decreases to 0.2 mm at 350 at. N. A. Afonina determined the change in the critical diameter of combustion of powdery tetryl at a relative density of ~ 1 depending on the pressure. The critical diameter greatly decreases with an increase in pressure, falling from 21 mm at 1 at down to ~ 1 mm at 30 at. According to I. V. Babaytsev, in conical tubes of quartz glass submerged into water, the combustion of PETN (with $p = 25$ at) is extinguished at 3.8, trotyl, at 4.6 and trinitrobenzene, at 6.2 mm.

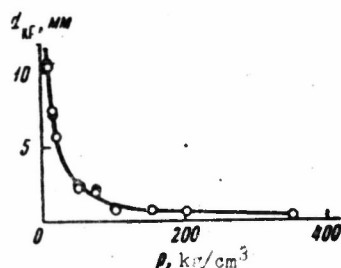


Fig. 86. Dependence of the critical diameter of combustion of cast trotyl upon pressure.

If one considers that the rate of combustion is approximately proportional to pressure and the surface of heat removal to the diameter of the tube, then results obtained for nitroglycol and trotyl can be interpreted as the constancy of relative heat losses with the critical diameter. Such a simple relationship can, however, be expected only with the identical type of combustion and the constancy of its thermal characteristics.

G. N. Beshpalov determined the critical diameter of combustion at atmospheric pressure of a number of specimens of powder on a nonvolatile diluent, which were different in composition (Table 15). The values of the diameter were different by more than 4 times and the rate of combustion (with diameters considerably more than critical), approximately 2 times. A certain conformity between the rate of combustion and critical diameter is revealed; however, there are many exceptions, which indicate that with respect to one rate of combustion of the powder it is still impossible to judge its capacity to burn. Beshpalov determined the capacity of powders to burn also at increased (20 at) pressure. Since it is difficult to prepare conical charges of very small diameters, he used wedge-shaped charges, armored by perchlorovinyl lacquer burned in an environment of water. The rate of combustion (Table 16) was more than that at atmospheric pressure, although at a different (3.6-8.9) number of times, the critical thickness of the wedge is less than the critical diameter at atmospheric pressure. Furthermore, a known conformity between the critical dimension and the rate of combustion is observed, although there are exceptions, especially when the composition of the powder is substantially different from the remaining ones (powder 6, for example, burned at the lowest rate with the least critical diameter).

The dependence of critical diameter upon the rate of combustion is more clearly exhibited in its dependence on pressure. On Fig. 87 this dependence is shown for two powders. For one of them the increase in the rate with pressure greatly weakens in the interval of 30-80 at correspondingly remaining almost constant in this region of pressure is the critical diameter of combustion; for another powder the rate increases and d_{kr} decreases. By the way, for both powders in the region of low pressures (up to 30 at) the rates of a combustion are close, and the values of critical diameter are somewhat different.

Table 15. Values of critical diameters and rates of combustion of a number of powders at atmospheric pressure.

Arbitrary designation of powder	Critical diameter of combustion, * mm		Rate of combustion, cm/s
1	1.8;	2.7	0.077
2	2.2;	3.4	0.120
3	3.5	4.5	0.066-0.069
4	4.1;	5.1	0.103-0.120
5	6.5;	7.5	0.053
6	7.3;	8.1	0.051
Powder N	9.0;	11.2	0.060

*See footnote in Table 13 on page 27.

Table 16. Values of critical diameters and rates of combustion for wedge-shaped charges of some powders at 20 at.

Arbitrary designation of powder	Critical diameter of combustion, mm		Rate of combustion, cm/s
1	0.18;	0.20	0.64
2	0.43;	0.50	0.43
3	0.39;	0.48	0.44
4	0.32;	0.38	0.73
5	0.63;	0.72	0.47
6	0.20;	0.34	0.22
Powder N	0.72;	0.80	0.30-0.37

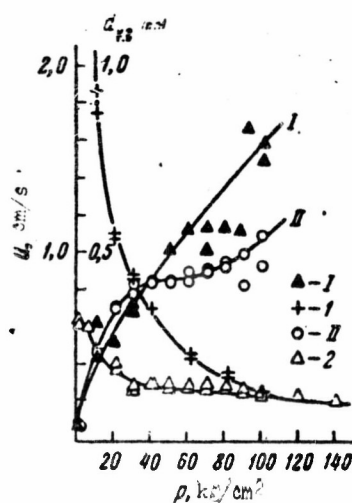


Fig. 87. Dependence of the rate and critical diameter of combustion upon pressure for two powders. I - $u(p)$, 1 - $d_{kr}(p)$ for powder I; II - $u(p)$, 2 - $d_{kr}(p)$ for powder II.

Let us note also that for powder 2, in determining the dependence according to curve $d_{kr}(p)$, it is possible more rapidly and simpler to estimate the character of the dependence $u(p)$ than by directly determining the latter.

From the aforesaid about the nature of the effect of pressure on the critical diameter of combustion it follows, that, by increasing the diameter of the tube, it is possible to obtain combustion at any amount of low pressure as desired.¹ In practice this, apparently, is not so for the reason that chemical conversion of the explosive during combustion at initial stages usually occurs with the absorption of heat and then cannot be self-propagating. The subsequent stages of conversion are exothermic; however, if the pressure is very small, then in practice they do not take place, and combustion becomes impossible. If we increase the pressure, then, by starting from certain limit (depending also upon external conditions), the process becomes totally exothermic and is capable of self-propagation.

Similar to the maximum critical pressure there can exist a maximum critical temperature (on which depends the finite temperature of the initial stage of conversion), especially, if the rate of exothermal reactions greatly depend on temperature. At higher temperatures combustion is possible but only with diameters exceeding the critical.

B. N. Kukib studied the effect of temperature on the capacity for the combustion of condensed hydrazines (from 3% diglycoldinitrate for the easing of pressing). The critical diameter, which decreases, although not very greatly, with the increase in the temperature, is 5.5 mm at +90°C and 6.5 mm at +15°C. The critical diameter of tetryl, according to experiments of N. A. Afonina, also decreases with an increase in temperature (Fig. 88) - two times with the change in

¹If we do not take into account the losses of heat by radiation which, according to Ya. B. Zel'dovich, determine the existence of the limit of capacity for combustion in the case of gas mixtures.

temperature from -20° to 90°C . In these experiments there was used a powdery tetryl at a density equal to ~ 1 , at which the possibility of combustion is greatly affected by the penetration of fusion into the depth of the powder, and the role of the fusion in turn can depend on the temperature.

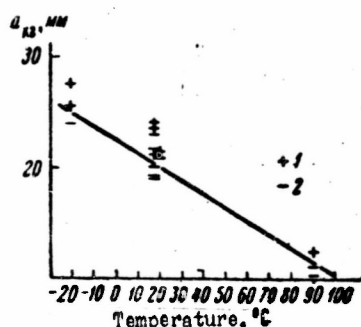


Fig. 88. Dependence of the critical diameter of combustion of tetryl upon temperature. 1 - tetryl burned; 2 - combustion extinguished.

With the congelation of a liquid explosive the critical diameter is increased. For example, gelatinized nitroglycerine burned in a tube with a diameter of 5.4 mm; to obtain its stable combustion in a frozen form it was required to increase the diameter of the tube to 11 mm. The effect of congelation is entirely understandable, since it similar to cooling, leads to a decrease in the rate of combustion and its heat (and, respectively, and temperature of the gases) by the magnitude of the latent heat of fusion.

Besides pressure and temperature, the possibility of combustion is affected still by a number of factors. Sometimes these factors are trivial. For example, during the combustion of methyl nitrate in a small glass tube lowered into water, on its walls vapors of water, which is formed during combustion are condensed. Drops of water, flowing downward, fall on the surface of the burning liquid and put out the combustion.

Less trivial is the extinguishment of combustion of the liquid, for example, nitroglycol with the jarring of the small tube in which combustion occurs. This jarring disrupts the heated layer of the liquid, which is adjacent to its surface during stationary combustion.

The heat removal into the depth of the liquid increases so much that it is not compensated by an increase in heat from gas products of combustion, and this leads to the extinguishment of the combustion.

Similarly, one should explain the extinguishment of combustion which was observed under known conditions with passage through the liquid of air bubbles. With the mixing of the heated layer with cold liquid (with passage of a bubble through the surface) combustion ceases.

Similar phenomena can be observed during the combustion of liquid (or melting) explosives if the combustion passes from the normal mode to the turbulent, at which the removal of heat into the depth of the substance and into the environment substantially increases. In this case a paradoxical phenomenon can be observed: the substance with a definite diameter of the charge burns at the low pressures, but the combustion is extinguished if the pressure exceeds a certain limit. Such a phenomenon was first established for liquid nitroglycerine [125] and for a solid nitromannite [126]. It was studied in more detail for nitroglycerine and some other nitroesters by Bepalov [127] and for PETN by Popova [123].

Experiments on nitroglycerine indicated that during turbulent combustion the critical diameter¹ even at relatively high (13-100 at) pressures is great - considerably more than that during normal combustion, and it increases greatly with a decrease in pressure. At 100 at it is 0.35 mm; with extrapolation at 1 at $d_{cr} = 14.5$ cm, while during the normal mode nitroglycerine can burn at atmospheric pressure with a diameter of the tube of 0.5 mm.

Inasmuch as pressure acts on the nature of the combustion of a liquid, the dependence of the critical diameter of the combustion of nitroglycerine upon pressure is more complex (Fig. 89) than that in

¹The critical diameter was defined usually as the diameter of extinguishment in conical tubes, which were narrowing (or expanding, see below) downward.

the absence of such an effect. In the region of the low pressures nitroglycerine is able to burn at relatively small diameters, for example, at 200 mm Hg in a tube with a diameter of ~ 1 mm. The increase in pressure, as usual, decreases the critical diameter, and in these conditions the combustion of nitroglycerine occurs in the normal mode - because of the small diameter turbulence is not developed.

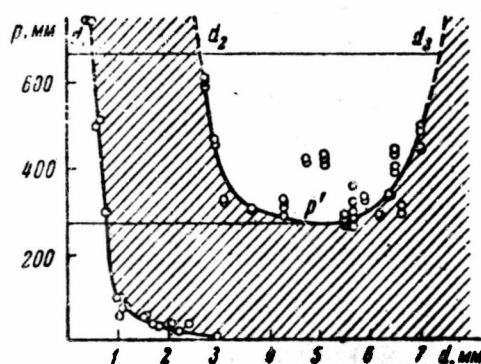


Fig. 89. Region of the combustion of nitroglycerine at low pressures (shaded).

If, however, at pressures higher than 30 mm, the diameter is increased above 3-4 mm, combustion is extinguished. The increase in diameter, on the one hand, is favorable for combustion propagation due to the decrease in relative heat losses; however, on the other hand, here the development of turbulence becomes possible. This latter effect prevails, and combustion is extinguished. With a further increase in diameter, the effect of the decrease in heat losses becomes greater than does the increase due to turbulence and combustion again becomes possible.¹

In favor of this explanation is the effect of gelatinization on the possibility of combustion. The increase in viscosity by means of gelatinization, which impedes the turbulization of combustion and lowers the region of its development to the side of high pressures, greatly decreases the critical diameter. Curve $d_{kr}(p)$ assume in this

¹For the providing of combustion of nitroglycerine at those values of the diameter and pressure at which it is possible, an important role is played by the method of ignition. The most, and under some conditions, singularly effective ignition was that at reduced pressure with a subsequent increase in the latter.

case a unique form (Fig. 90). In the region of the small pressures where combustion occurs in an undisturbed mode, the critical diameter decreases (the section of curve of 1-10 at); the appearance of turbulence in pressures above 10 at leads to an increase in critical diameter (the section of curve of 10-30 at); at higher pressures the effect of the decrease in heat losses prevails and d_{kr} again drops. The more viscosity of the gelatin, the weaker the increase in critical diameter conditioned by turbulization is expressed.

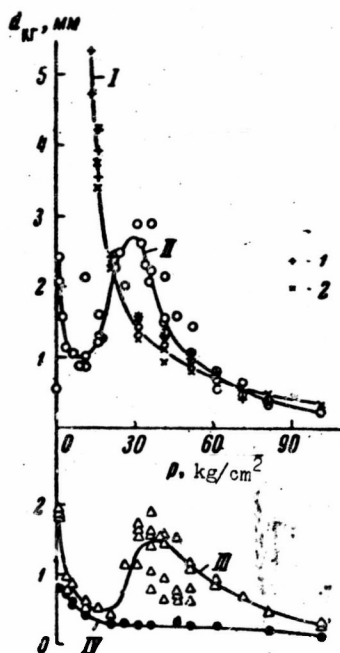


Fig. 90. Dependence of the critical diameter of combustion (d_{kr}) of nitroglycerine and its gelatin upon pressure (p) in the interval higher than atmosphere. I - nitroglycerine (1 - in an environment of air, 2 - in an environment of water); II - 3.2% gelatin; III - 5% gelatin; IV - 8.5% gelatin.

Experiments on the determination of d_{kr} at different pressures were also carried out for nitroglycol. It was expected that during the transition to a turbulent mode the interval of pressures where combustion will be extinguished is detected. This, however, was not observed, although near the corresponding pressure, if turbulent combustion was immediately started, the extinguishment frequently occurred with much greater diameters than in its absence (Fig. 91).

The extinguishment of combustion or of the apparent increase in critical diameter and during the transition into the turbulent mode of the combustion of dinitroglycerine was not observed (Fig. 92).

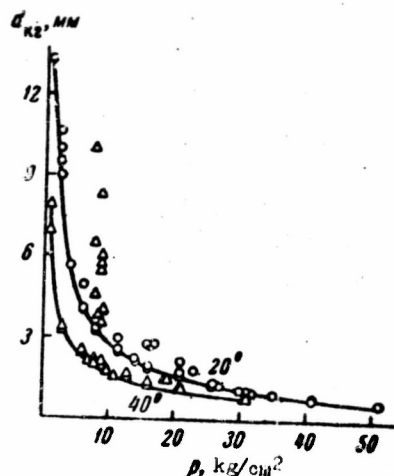


Fig. 91.

Fig. 91. Dependence of the critical diameter of combustion of nitroglycol upon pressure at 40 and 20°C.

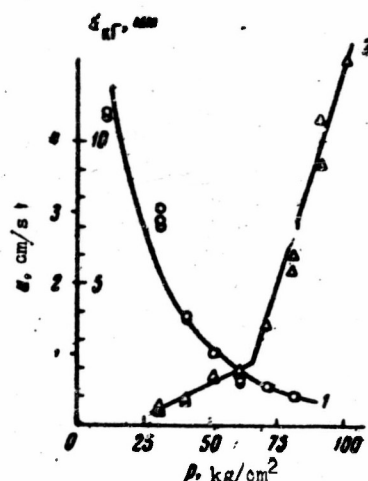


Fig. 92.

Fig. 92. Dependence of critical diameter and rate of combustion of dinitroglycerine upon pressure. 1 - $d_{kr}(p)$; 2 - $u(p)$.

The extinguishment of combustion with an increase in pressure was observed also in a solid nitroester - PETN. It was known that with the diameter of the tube of 6 mm PETN is able to burn at atmospheric pressure and a moderately increased temperature (100°C). At room temperature, however, combustion was not propagated. The probable reason for this was the large critical diameter. Actually, with an increase in the diameter up to 30 mm combustion ($\rho = 1.2 \text{ g/cm}^3$) became possible; the rate of combustion is small ($0.023 \text{ g/cm}^2\text{s}$). However, at somewhat increased pressures PETN with this diameter of the tube did not burn. With ignition in a semiclosed container (a bomb with an open valve) the loss of the ability to burn at increased pressures appeared uniquely. The PETN was ignited at atmospheric pressure, when the pressure because of gasification was lowered to 2.5 at and combustion was extinguished. As a result of the outflow of gases through the valve the pressure fell and the PETN (the igniting spiral was not turned off) was again ignited, and extinguished and this was repeated several times.

The extinguishment of the combustion of solid PETN but melting during combustion should be explained by turbulization of the molten part of the heated layer, which leads to an increase in heat losses. At the small rate of combustion this increase proves to be sufficient for extinguishment. Just as in nitroglycerine, the absence of the ability to burn is exhibited with PETN only in some interval of pressure in given conditions of the experiment - up to 16 at. At high pressures PETN burns, but the burning rate, unlike nitroglycerine, corresponds to normal combustion: the thickness of the molten part of the heated layer at a considerable rate of combustion, which corresponds to the increased pressure, is small, and this limits the development of turbulence in it. On the other hand, in view of the achievement of the completeness of combustion (up to nitrogen instead of NO) the heat arrival of conversion is increased.

The extinguishment of combustion of PETN with an increase in pressure (up to ~2 at) was observed at increased initial temperature (100°C, $d = 7$ mm). The extinguishment of combustion occurred when PETN was ignited at an increased pressure (20 at) and then the pressure was slowly decreased; it approached at ~10 at (the experiment was carried at 20°C).

Experiments with the fusion of PETN at 140°C indicated that the combustion at 8-9 at passes over to a pulsating mode; extinguishments in this case are not observed, just as with the combustion of other nitroesters at increased pressures and temperatures. The rate of pulsating combustion, naturally, is much more than that obtained with the extrapolation of experimental data during undisturbed combustion. With gelatinized (polymethylmetacrylate) the fusion of PETN combustion passes over to a pulsating mode at somewhat greater pressure (9-13 at).

The extinguishment of combustion with an increase in pressure was also observed during the combustion of liquid hydrazine [124]. The rate of combustion of hydrazine increases approximately in proportion to the square root of the pressure. Above 10 at the data are reproduced worse, and the mean values approach a certain constant, not

dependent on pressure. Above a certain pressure the liquid will not be ignited from an incandescent wire. Extinguishment was observed when the liquid was ignited at low pressures, and then the pressure was raised. Critical pressure depends on the diameter of the tube, increasing from 22 to 34.5 at with its increase from 3 to 5 mm, and it is decreased with the dilution of hydrazine by water. The decreases in the rate of combustion before extinguishment was not observed.

Investigators explain the extinguishment of combustion by the following considerations. The pressure of extinguishment in tubes with a diameter of 5 mm is directly proportional to the rate of combustion at atmospheric pressure. Correspondingly, it can be considered that the pressure of extinguishment depends on the rate of the flow, the density of the gas, and also diameter of the tube, and that this effect has a hydrodynamic nature. Inasmuch as the mass rate of combustion is proportional to the square root of pressure, the rate of the flow of unburned vapors near the surface of the liquid decreases with an increase in pressure. Near the limit of the extinguishment it is comparable in magnitude to the convectional rates which can, appearing on account of the fact that the density of the products of combustion is small in comparison with the surrounding air, remove the flame from the surface of the liquid. As a result of this side heat losses are increased, and the propagation of combustion becomes impossible. If this reason is real, then the decrease in density of the surrounding atmosphere should have hampered the extinguishment, which was also observed during the replacement of nitrogen by helium. In nitrogen the pressure of the extinguishment was 8-9 at, and, in helium combustion was continued at 13 at.

The extinguishment of the combustion of hydrazine is very similar to phenomena during the combustion of nitroglycerine. Unfortunately, experiments with hydrazine were not conducted at high pressures when (if the similarity with nitroglycerine is not accidental) it would be possible to expect the renewal of combustion but already in the increasing mode.

Let us discuss the effect of fractional gratification during combustion, the value of which we explain in the example of combustion of the stoichiometric solution of the liquid components not burning independently, which are *greatly different in volatility*. With the ignition of such a solution in the beginning, naturally, predominantly the more volatile component will be evaporated, and over the surface of the explosive a low-calorie mixture of vapors is formed. Only after the surface layer of the liquid is enriched with a difficultly volatile, component into a gas phase there will begin to enter a mixture of the composition which corresponds to the maximum caloricity, the combustion of which is in a state to sustain combustion. Combustion of the substance will be hampered because of the heat consumption for the elimination of the highly volatile component. Hampered also will be subsequent combustion, inasmuch as the volatile component will have to enter from the deep layers, by diffusion or by another way. Thus, the difference in the volatility of interacting components of mixture will lower its capacity for combustion.¹

Similar phenomena can be observed during the combustion of a mixture consisting of nonvolatile components, which are decomposed independently of each other and at greatly differing rates. Then one of them (for example, fuel) will be decomposed earlier than another (oxidizer), and when the temperature on the surface becomes sufficient for the decomposition of the oxidizer, the fuel will have to enter for participation in the reaction of deep layers.

Furthermore, the deviation in the composition of the gas phase with combustion from the composition of explosives is possible even with the combustion of individual explosives. It is known that for organic nitrates, and, apparently, for nitrocompounds of an aromatic series, the initial stage of dissociation is the cleavage of the nitric dioxide, for the majority of explosives more volatile than the remaining part of the molecule. Thus, the synchronism of the

¹Such a phenomenon was first discovered and studied by A. I. Golbinder in an example of the mixture of benzene with tetranitromethane [128].

dissociation and interaction of components of the mixture or groups determining the heat release in the molecule of individual explosives is an important factor of the capacity for combustion and, specifically, combustibility of the explosives.

Besides those described, there is still a number of observations on the extinguishment of combustion, which have not as yet obtained a reliable theoretical explanation. Thus, the potassium picrate burns at atmospheric pressure at high speed but loses this ability at 500 mm, although the rate of combustion is still great, and it is difficult to explain the fading effect of the combustion by heat losses. This refers to picrates of a number of other metals, for example, sodium, which do not burn at atmospheric pressure. At the same time the other rapidly burning explosives burn stably at much lower pressures, for example, fulminating mercury burns at 20-10 mm and lower, tricycloacetone peroxide - at 40 mm, trinitrotriazido-benzene - even at 10 mm.

The mixtures of styphnate of lead in a powdery form with a large content of talc do not burn, and with its small content they give a flash; it is impossible to obtain a stable combustion with moderate rates. The mixtures of lead styphnate with nitrocellulose (also in a powdery form) burn stably if the content of styphnate is not too great; otherwise combustion turns into an explosion. Mixture of trinitrotriazidobenzene with lead styphnate in a pressed form stably burn at atmospheric pressure with a content of up to 20% of the latter. At 30-40% combustion is not propagated; 60-70% mixtures again prove to be capable of combustion

The probable reason for the extinguishment in the described examples consist in the extreme intensity of dispersion of the condensed phase: the quantity of a solid entering into the zone of hot gases and cooling them becomes so great that the propagation of combustion proves to be impossible.

For the determination of the critical diameter of combustion of the ammonium perchlorate was used the finely dispersed product of

plant grinding, which was placed into the glass tubes submerged into water. At small density (0.6 g/cm^3) extinguishment occurred¹ if the diameter of the tube was equal to 26 mm, and at great density (1.0 g/cm^3) - 33 mm.²

One should add that attempts to reproduce these results with pure perchlorate pulverized in mortar, were not successful: perchlorate did not burn even with the diameter of the charge at 40 mm.

It is possible therefore that the aforementioned specimen contained some admixtures, which substantially increased the ability to burn. Experiments produced on a laboratory specimen at 30 at indicated that the critical diameter of its combustion is 10 mm. The addition of fine-grained aluminum greatly decreases the critical diameter.

Organic admixtures increase the ability of perchlorate to burn. The effect of density is observed for these mixtures. The mass rate of a combustion is not considerably affected both in the case of perchlorate and its mixtures by condensation.

Thus, unlike some compositions on the basis of ammonium nitrate, condensation decreases the ability of the ammonium perchlorate to burn. It is possible that this distinction is connected with the fact that ammonium perchlorate, unlike ammonium nitrate, during combustion are not melted. On the whole these data indicate that the ammonium perchlorate is characterized by a relatively low ability to burn, being inferior in this respect to trotyl but substantially exceeding ammonium nitrate.

¹With the combustion of perchlorate on the internal walls of the tube, there remains a layer of unburned substance, which is especially thick if the tube is surrounded with water. In conical tubes this layer with a decrease in diameter of the section of the tube becomes thicker and at the moment of extinguishment is close to the radius of the section. Combustion itself occurs on the end of the charge unevenly - in the form of a focus (or several foci) with a diameter of 3-5 mm, which moves along the surface. The surface of the extinguishing charge is uneven speckled with cavities.

²In these conditions d_{kr} of hydrazine is 8 mm.

For ammonium perchlorate with a small transverse dimension of the charge, there is observed not only the lower limit of the ability to burn with respect to pressure but also the upper limit [129].

With the increase in diameter of the charge, according to experiments of Glazkova [130], the lower limit of pressure is lowered,¹ and the upper limit rises; at 250 at d_{kr} is (for bare charges) about 5 mm. The existence of the upper limit for ammonium perchlorate is connected, apparently, with the fact that with an increase in pressure in its definite interval the rate of combustion, instead of continuing to increase, starts to decrease.

Such an explanation required, however, confirmation of the fact that decrease in the rate of combustion with the increase in pressure is the reason for the increase in heat losses and not the consequence of this increase, which can be connected, for example, with the increase in density of the surrounding gas, the intensification of convection, etc. For this the rate of combustion was determined for charges which were located in a plastic (plexiglass) tube, which was rather well thermoinsulated them from the environment.² The decrease in the rate of combustion in the range of 160-200 at was observed in this case (Fig. 93), thus confirming the dependence of the drop in the

¹According to Levy and Friedman, on the other hand, the lower limit, equal according to their experiments for columns of square section (4×4 mm) with an intense combustion 22 at, does not depend on the dimensions of the specimen; it also does not depend upon whether the surrounding atmosphere is nitrogen or helium; they connect this with the fact that supposedly the determining role is played by heat losses because of radiation and as an additional argument indicate that the specimen cooled down to -18°C of perchlorate did not burn even at 270 at.

²The interpretation of results of this experiment requires one reservation; the material of the shell (plexiglass) and the burning ammonium perchlorate can interact with each other; this possible interaction introduces a new factor into the phenomenon, the effect of which is difficult a priori to evaluate. However, judging from the fact that the mixtures of the powdery plexiglass with perchlorate in the given range of pressure burn more slowly than the perchlorate itself, their interaction with an incomparably less close contact - the charge with the wall - can hardly play a significant role.

rate of heat losses into the environment. Additionally this conclusion is confirmed also by experiments on combustion with various diameters of the tube (5, 7 and 10 mm), which did not indicate a distinction in the rate of combustion.

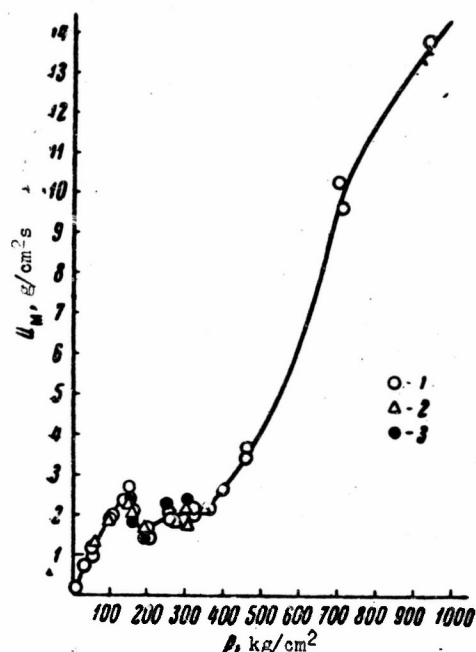


Fig. 93. Dependence of the rate of combustion on pressure for ammonium perchlorate pressed into plexiglass tubes of different diameter. 1 - $d = 7$ mm; 2 - $d = 5$ mm; 3 - $d = 10$ mm.

Similar experiments of Levy and Friedmann were conducted somewhat differently in the method of execution [131]. They burned columns of perchlorate in an asbestos winding, and did not detect up to the studied limit of pressure (340 at) of the cessation of combustion or the decrease in rate. The authors arrived at the conclusion, apparently, without sufficient bases, that the upper limit of the ability to burn according to the pressure of the bare charge is conditioned by convective heat losses.

A unique effect on the lower limit is exerted by the addition of a catalytic agent, for example, copper chromite (Fig. 94). A great addition lowers it, which, naturally, is explained by the increase in the rate of an exothermal gas-phase reaction; on the contrary, little addition, even a total of 1:20,000, greatly (4 times)

increases the lower limit, which authors explain by the increase in the radiating ability of the zone of combustion and, consequently, heat losses.

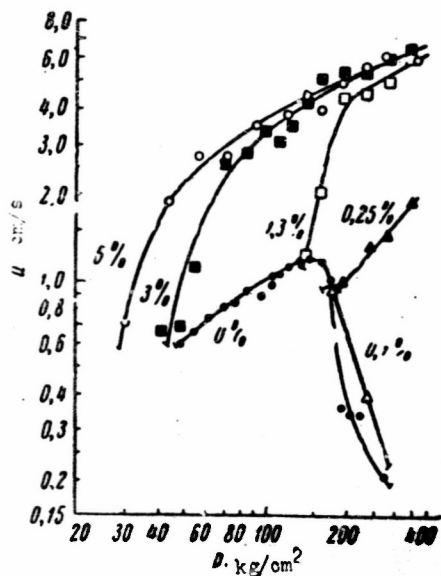


Fig. 94. Rate of combustion of ammonium perchlorate with a different content (numbers by curves) of cuprous chromite.

Conclusions

The combustion of a column of explosives is possible only when the heat losses of a burning layer do not exceed the certain limit at which the stable equilibrium between the increase in heat and heat emission in this layer is broken. In accordance with this the change in conditions of combustion to the side of the increase in heat losses or decrease in the heat arrival can lead to the fact that combustion will become impossible.

The basic of these conditions are the diameter of the charge (with the combustion of a column of explosives on the end), pressure, temperature and cubic density (for powdery explosives). Correspondingly there exist a critical minimum diameter, minimum pressure and minimum temperature, lower than which combustion is not propagated

The values of these parameters are not absolute characteristics of explosives but reciprocally connected. The possibility of the

combustion is also affected by the thermal conductivity and the thickness of the shell. The cessation of combustion can appear, further, under all conditions, which lead to the breakdown of the heated frontal layer of the explosive.

III. Effect of Pressure on the Rate of Combustion of Explosives

The dependence of the rate of combustion of explosives upon external pressure is one of two basic theoretically important characteristics of combustion. Simultaneously it represents a considerable technical interest. Stable combustion of a charge in a semiclosed volume is possible only when the rate of combustion increases with pressure more slowly than the rate of the outflow of gases through the nozzle proportional to the pressure. With a strong dependence of the rate of combustion upon pressure, its tendency toward a transition into an explosion is usually higher.

The rate of combustion, as a rule, increases with an increase in pressure. This is quite natural when exothermal reactions during combustion occur in the gas phase. The increase in pressure by increasing the absolute rate of these reactions, approximates the zone of their passage the surface of the condensed phase and increases the temperature gradient near this surface and, respectively, the heat transfer of the latter.

This basic effect of pressure on the rate of combustion agrees with that fact that for a number of explosives, which are characterized by low volatility, where it is proposed that exothermal reactions occur in a condensed phase, the rate of combustion does not depend on pressure.

The lack of such a dependence was observed in smokeless powder with a great lowering of the pressure and was explained by the fact that in these conditions the rate of the gas-phase reactions decreased so much that the portion of these reactions turning into the heat obtained by the surface of the condensed phase became negligible in comparison with the heat separable by reactions occurring in the condensed phase. In known conditions, however, the acceleration of combustion with an increase in pressure can

occur also independently of its effect on the rate of the gas-phase reaction: as a result of the increase in density of the gas phase the quantity of the heat transferred to the surface of the condensed phase increases.

The considerable decrease in the rate of combustion with an increase in pressure observed in some explosives is less understandable. It is possible that this decrease is connected with the hindering of the dispersion of the substance during combustion or with the effect of the sound vibrations, which appear during combustion, on its flow.

All these diverse forms of the dependence of rate upon pressure have one important general feature: the rate of combustion usually increases more slowly than that of pressure (if we exclude brief (in the interval) pressures of the section of transition from the constancy or drop in rate to its increase). If in the experiment du/dp increases with pressure, then this is almost always a criterion of the fact that combustion passed from the normal into the disturbed mode.

The basic forms of the disturbed combustion are the turbulent combustion of fluid and a convective combustion of solid porous explosives.

For all the studied fluids, normal combustion on the reaching of a definite pressure passes over to pulsating mode. If this transition occurs at very low pressures, then it can lead to the extinguishment of the combustion; at high pressures a great increase in the rate and its more rapid increase with pressure are observed. The pressure of the transition to a great degree depends on the rate of the combustion inherent to the given substance, decreasing with its increase. Correspondingly, in the quick-burning nitroglycerine the change in modes of combustion occurs at 0.5 at and in slowly burning diglycol dinitrate - 55 at. By the increase

in the viscosity of the fluid, for example, by the dissolving in it of a high polymer, it is possible to greatly expand the interval of the stability of normal combustion with respect to pressure

In powdery (more accurate by gas-permeable) explosives, in exactly the same manner there is observed a certain limit of pressure, higher than which normal combustion turns into the mode connected with the penetration of gaseous products of combustion into the depth of the charge. Both of these types of disturbed combustion will be examined further.

It is difficult to express mathematically by a single equation the various types of dependence $u(p)$ because even for the same substance in different intervals of pressures the nature of the dependence is often different. Appropriate expressions $u(p)$ bear the empirical nature and are applied therefore only for that interval of the pressures in which they are determined. We will examine some of them in reference to specific explosives.

The simplest and most widespread in the theory of combustion is expression $u = A + Bp$, and for many substances term A is relatively small, so that dependence $u(p)$ approaches to the direct proportionality. The linear dependence was established [132] in the region of relatively low pressures for methyl nitrate, nitroglycol (liquid and gelatinized), gelatinized nitroglycerine, diglycol nitrate, nitrocellulose, hexogen, tetryl and fulminating mercury. In the expansion of the interval of pressure upward (for individual explosives up to 1000 at) the linear dependence for a number of explosives is retained although with somewhat different coefficient. The number of these explosives refer to PETN trotyl and picric acid.

For some explosives (tetryl, hexogen, powders on a difficulty volatile solvent) curve $u(p)$ in the interval of pressures from several to 100-250 at is evidently diverted from a straight line: the rate increases more slowly than proportional to the pressure and

can be approximately expressed by relationship $u = A_1 + B_1 p^v$, where A_1 and B_1 - constants, and v is less than unity. Above a certain limit of pressure the rate starts to increase linearly: $u = A_2 + B_2 p$, and $A_2 > A_1$.

For substances of the third group (fulminating mercury, black powder) the saturating increase in the rate of combustion with pressure is retained in the whole studied interval of the latter.

For a number of quick-burning explosives the rate of combustion in the region of low pressures rapidly increases, and then this increase is greatly retarded or even entirely ceased. The examples of such substances can be picrates also styphnates of lead.

Finally, for some explosives the rapid increase in the rate in the field of low pressures then passes over into its more or less considerable drop, which with a further increase in pressure again changes by a relatively gradual slow increase. Thus, for example, the potassium picrate and ammonium perchlorate behave this way.

The increase in pressure is usually accompanied by a change in composition of the products of combustion, which at high pressures corresponds to chemical equilibrium; at low pressures the products of combustion contain many components, which indicate the incompleteness of the conversion, typical of which for nitrates and nitro compounds is nitric oxide. In products of combustion the nitroglycol at atmospheric pressure the ratio of the content of nitric oxide to the sum of the contents of carbon-containing gases ($CO_2 + CO + CH_4$) is equal to 0.9, i.e., almost the entire nitrogen is liberated in the form of NO; at 9 at this ratio is 0.7, and at 14 at the nitric oxides in the products of combustion is absent.

For some explosives (nitroglycol, nitroglycerine and others) the change in the composition of products of combustion with an

increase in pressure is sharp and is accompanied by the appearance of a secondary flame, in which, obviously, there is the interaction of the nitric oxide with the ignitable products of the initial stages of conversion. It is possible that for other explosives, for example, nitrocellulose [133], a transition from combustion up to NO to combustion up to elementary nitrogen is somewhat expanded with respect to pressure.

The pressure at which there appears the secondary flame is not identical for the studied nitroesters and, furthermore, depends upon the diameter of the charge, decreasing with its increase. For nitroglycol with a diameter of 5 mm the flame appears at 9.5 at and with a diameter of 9 mm - 5.6 at. For diglycoldinitrate (liquid or slightly gelatinized) the secondary flame appears more difficult: with a diameter of 5.2 mm it is at 16 at and, with a diameter of 10.5 mm - at 7.5 at. With nitroglycerine gelatin (3-5% collxylin experiments were conducted in tubes of smaller diameter (~ 3 mm), and secondary flames appear at higher pressure (15 at); however, its limit at low pressures is very uneven as a result of the frequent approach to the initial flame, and only starting with 30 at does it acquire clear outlines. At an even greater pressure (35-40 at) a secondary flame appears during the combustion of ethyl nitrate.

The change in initial temperature of the gelatin nitroglycol of 40° (from 20° to 60°C) was practically not reflected on pressure at which the secondary flame appears. Apparently, the processes leading to its formation occur at comparatively high temperatures, with respect to which its indicated change is small.

Some mineral impurities in small quantities (1%) greatly (two times) lower the pressure at which the secondary flame appears, and others, on the contrary, somewhat increase it. The rate of combustion at this pressure in both cases was lower than in the absence of impurities. Correspondingly higher in the presence of

impurities was the limit of pressure, starting from which combustion became possible.

The second important characteristic of double-flame combustion is the distance of the initial flame from the secondary one and the change in this distance with pressure. These data for the liquid and gelatinized nitroglycol [271] is presented in Fig. 95; for nitroglycerine gelatin the distance is considerably greater than that for nitroglycol, which can be connected with the greater rate of combustion of the latter; in a comparison it follows, however, to take account that the diameters of the charge in both cases were different.

With solid PETN the secondary flame is absent at atmospheric pressure, and the products of combustion contain about 40% of nitric oxides. At 16 at the nitric oxides are not contained in the products of combustion, but the secondary flame is located so close to the initial one that the interval between them is indistinguishable; this, nevertheless, to a certain extent can be connected with the relatively small rate of combustion of PETN in conjunction with the high temperature attainable in the secondary flame.

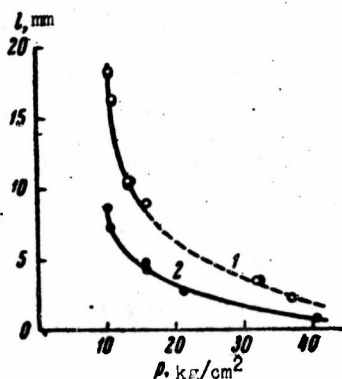


Fig. 95. Change in distance between the initial and secondary flames with pressure. 1 - liquid nitroglycol; 2 - gelatinized nitroglycol. The dashed line denotes the region of the pulsating combustion.

The distance between the secondary and initial flame also depends upon the initial temperature of the explosive: it increases with its increase. This, apparently, is connected with the fact that the temperature of the processes which lead to the formation of the secondary flame are much higher than the leading

temperature of the initial flame; therefore, the increase in temperature by the same magnitude proves to be for the secondary flames relatively less than that for the initial flame.

Inasmuch as the final temperature of the initial flame in the absence of heat losses can be calculated, the determination of the effect of the initial temperature on the induction period of the appearance the secondary flame can be used for the calculation of the kinetic characteristics of this process.

Double-flame combustion was detected by Zeldovich and Shaulov with the combustion of vapors of methyl nitrate [134]. The second flame appears only with the considerable compression of the products of initial dissociation in the same way as it takes place during the combustion of liquid nitroglycol at increased pressures. Unfortunately the first flame could not be photographed in view of its weak light emission, and therefore it was impossible to establish accurately the rate of combustion of the vapors.

1. Nitroesters

The research of the dependence $u(p)$ for nitroglycerine is impeded by the fact that the combustion of this liquid explosive at low (<1 at) pressures passes over to a turbulent mode which usually causes its extinguishment.¹ Therefore, the indicated dependence was directly determined only in the interval of the pressures of 20 to 300 mm, $u = 0.0067 + 0.216 p^{0.831}$. From this equation it was easy, in particular, to calculate the rate of combustion at the pressure of extinguishment equal to 0.072 cm/s; the rate directly measured near the pressure of the extinguishment was 0.077 cm/s.

Experiments with nitroglycerine were also conducted at increased temperatures (98°C). The pressure, starting from which

¹Critical pressures depend on the diameter of the tube, see page 41.

combustion with firing does not appear is approximately the same: 320-380 mm. However, at increased temperatures the rate of combustion, naturally, is more; therefore, and the maximum rate near the extinguishment is more and constitutes about 0.13 cm/s. Furthermore, if the pressure during combustion increases up to the critical, then combustion does not always or in any case is not at once finished by extinguishment. The first stage with an increase in pressure is the pulsating combustion, and in some experiments it is unique: it is as if the flame had penetrated along one side of the wall of the tube at a great depth, and the front of combustion of the fluid becomes almost vertical. It is possible that this phenomenon is a pulsation of a very great period.

By extrapolating the curve $u(p)$ on high pressures, it is possible to calculate the rate of combustion at atmospheric pressure equal to $0.23 \text{ g/cm}^2\text{s}$. This magnitude corresponds to results of the direct measurement of the rate of combustion at atmospheric pressure in tubes with a diameter of 0.5-1.5 mm. Attempts were made to determine the rate of combustion by the following way: if we add to nitroglycerine 2% pyroxylin No. 1, then it is ignited comparatively easily and burns at atmospheric pressure at the rate of $0.28 \text{ g/cm}^2\text{s}$.

Experiments at reduced pressures showed that an admixture of 2% pyroxylin does not have a noticeable effect on the rate of combustion of the nitroglycerine. If this would be correct for atmospheric pressure, then it would be possible to conclude that the rate of combustion of nitroglycerine is equal to $0.28 \text{ g/cm}^2\text{s}$. However, in comparing this magnitude with the obtained extrapolation and direct determination, one should conclude that 2% pyroxylin incompletely suppresses the agitation during combustion at atmospheric pressure, and that the indicated rate is somewhat overstated.

An attempt to determine the rate of the combustion of solid nitroglycerine is impeded by the fact that the critical diameter for it is much more than that for the liquid. Therefore, a

determination was carried out at 27 at; the rate of combustion was equivalent to $2.68 \text{ g/cm}^2\text{s}$, i.e., much less than that for a liquid because of the distinction of modes of the combustion and partly because of the lower temperature of the combustion. In gelatinized (2% colloxylin) form nitroglycerine ($d = 11 \text{ mm}$) at $+9^\circ\text{C}$ and atmospheric pressure burned in a nonfrozen state at the rate of 0.113 cm/s and in a frozen state - 0.0838 cm/s .

The increase in viscosity by means of dissolving a high polymer increases the ability of nitroglycerine to burn. The rate of combustion (at atmospheric pressure) decreases from the beginning considerably, and with a further increase in a high-polymer content it is much weaker. Thus, with the dissolving of 1% colloxylin it decreased down to 0.02, during the transition from 1 to 2% only 0.006, and from 2 to 3% - 0.001 cm/s. A distinction in the rate does not appear noticeably at the low pressures, when owing to the low rate of combustion the nitroglycerine itself burns in a normal mode at an increase in pressure the combustion of nitroglycerine dies out (Fig. 96), and the low-viscosity solutions burn with an increased rate as a result of the appearance of agitation; at an even greater pressure they are extinguished.

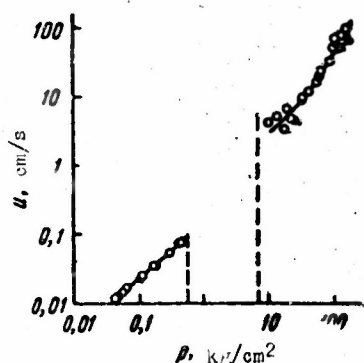


Fig. 96. Dependence of the rate of combustion of nitroglycerine upon pressure.

By the application of colloxylin of different viscosity and by the comparison of the ability to burn up to and after the solutions of the high polymer and also solutions of a monomer and polymer, it was shown [135] that the effect of the latter has

not a chemical but physical nature. The increase in viscosity impedes the formation of turbulence and increases the pressure of the transition from a normal to a disturbed combustion. Owing to this, the determination of the dependence of the rate of combustion upon pressure in an interval of the latter larger than that for a liquid becomes possible. From 0.3 to 2.2 at this dependence for 3% colloxylin gelatin can be expressed by the linear equation $u_n = 0,0315 + 0,146 p$. In a wider (up to 150 at) interval of pressures the dependence $u(p)$ was determined by G. N. Bepalov for gelatins containing 3.2, 5 and 8.5% colloxylin (Fig. 97). In this range of content of the high polymer the rate of combustion is noticeably not changed. Its increase with pressure, especially in the region of moderately increased pressures (up to 30 at), distinctly slows down.

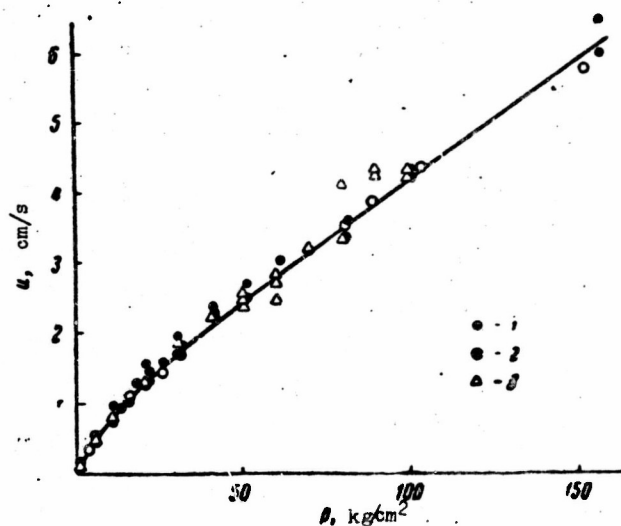


Fig. 97. Dependence of the rate the combustion of nitroglycerine gelatins upon pressure. Colloxylin content (%): 1 - 3.2; 2 - 5; 3 - 8.5.

The other studied liquid nitroesters (methyl nitrate, nitroglycol, diglycolinitrate and ethyl nitrate) burn more slowly than the nitroglycerine. Correspondingly, the interval of pressure in which combustion occurs in a normal mode, for them is more: for methyl nitrate, up to 1.75, for nitroglycol up to 20, for diglycol dinitrate

up to 55, and for ethyl nitrate, up to 80 at. The rate of normal combustion at the pressures of the transition for the last two explosives is respectively, 0.6-0.7 and 0.5 cm/s. At small intervals of pressure near atmospheric the rate of combustion can be expressed by linear equation $u = A + Bp$ (Table 17), and term A is small in comparison with B , and correspondingly the dependence is close to a direct proportionality.

Table 17. Values of coefficients A and B in the equation of combustion $u = A + Bp$ for some nitroesters.

Substance	Interval of pressure in which the equation is valid, mm Hg.	A	B
Nitroglycol	300-770	0.005	0.0375
Nitroglycerine	20-300	0.0067	0.216
Gelatinized 3% nitroglycerine	200-1600	0.0315	0.146
Methyl nitrate	130-1520	0.010	0.133

*For nitroglycerine: $u = A + Bp^v$, $v = 0.81$.

Thus, for instance, for nitroglycol between 0.4 and 1 at $u_n = 0.005 + 0.0375p$. In a wider interval of pressures, especially near the transition to disturbed mode, the rate of combustion increases somewhat faster; at the pressure of the transition the nature of the combustion is substantially changed. The surface of the liquid clearly ceases to be calm and horizontal, the whole combustion is as though it were a series of flashes rapidly following after each other, and the rate of combustion sharply increases and fluctuates within great limits. The tendency of combustion toward the transition into an explosion in this region of pressure substantially increases.

Photographic recording of pulsating combustion is distinguished by the fact (Fig. 98) that the distance between the initial and secondary flames does not remain constant. The secondary flame

through identical or dissimilar time intervals approach the surface of the liquid and then is withdrawn from it. Apparently, agitation on the surface of the burning liquid leads to the cooling of the heated layer, and vaporization slows down. Then the band of the secondary flame approaches the surface. Meanwhile, the heated layer manages to be restored and possibly even becomes thicker than normal; vaporization and initial combustion are intensified; the rate of the withdrawal of their products increases, and the secondary flame is rejected from the surface of the liquid.



Fig. 98. Photograph of pulsating combustion of liquid nitroglycol in a tube with a diameter of 3.5 mm. 1 - initial flame; 2 - secondary flame.

At even higher pressures the combustion again acquires an apparent uniformity but proceeds at a rate one order higher than at normal combustion.¹ (Fig. 99).

The more detailed research of S. V. Chuyko of the transient region showed that the change from the straight line $u(p)$ for

¹According to experiments of S. V. Chuyko, for nitroglycol the maximum pressure of normal combustion is somewhat decreased with an increase in diameter of the tube; at the same time du/dp during combustion in a rapid mode also depends upon the diameter of the tube increasing with its increase from 4 to 7 mm; for diglycol dinitrate and ethyl nitrate this effect of the diameter is not observed.

normal combustion to the straight line¹ of turbulent combustion occurs along a complex curve. For nitroglycol the rate in this region is more than this would correspond to the straight line of turbulent combustion (Fig. 100); for diglycol nitrate and ethyl nitrate in narrow tubes (4-5 mm) it proves to be somewhat lower. These characteristics, apparently, are connected with the double effect of agitation on combustion - disrupting the heated layer, it impedes combustion and it can even lead to its extinguishment, as is observed for nitroglycerine at low pressures. On the other hand, by increasing the surface of contact between the gas products of combustion and liquid agitation can accelerate the combustion. Depending on the thermal kinetic characteristics of the substance and also the region of pressure where agitation approaches, a certain effect can prevail. For the thickened means of gelatinization of the liquid, the pressure of the change in the mode of combustion greatly increases, and up to 150 at nitroglycol of the gelatin burns at a normal rate, linearly growing with the pressure (Fig. 101), just as for nitroglycerine, somewhat smaller than the normal rate of the combustion of nonthickened liquid.

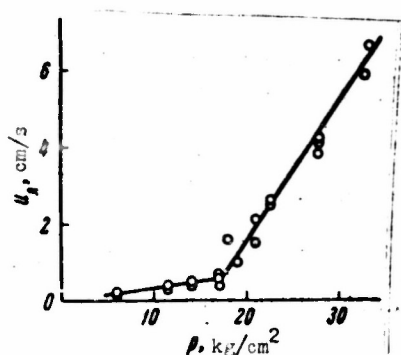


Fig. 99. Dependence of the rate of combustion of liquid nitroglycol upon pressure [271].

Solid PETN, not burning at the moderately increased (2-16 at) pressures in tubes of small diameter, acquires this ability at high pressures. The rate of the combustion from 16 to 1000 at increases

¹For diglycol dinitrate line $u(p)$ in the section turbulent combustion has a certain convexity turned to the axis of the ordinates.

in proportion to the pressure, and the coefficient of proportionality of 1000 at is approximately the same as that at 1-2 at.

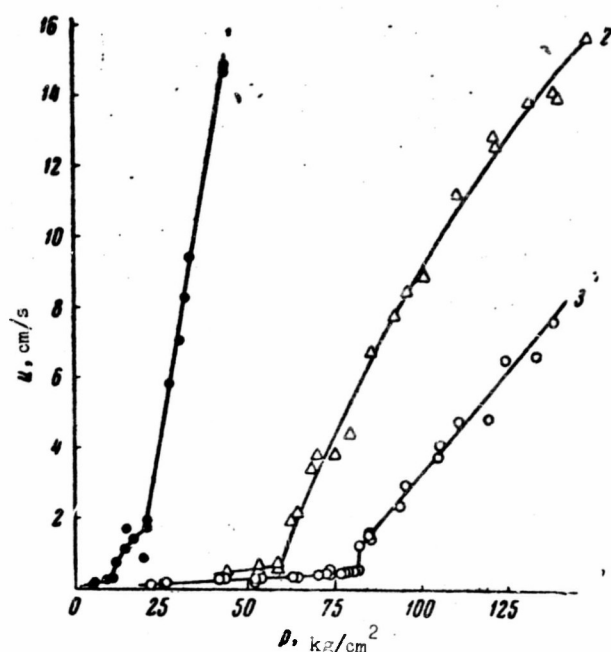


Fig. 100. Dependence of the rate of combustion of certain nitroesters upon pressure. 1 - nitroglycol; 2 - diglycol nitrate; 3 - ethyl nitrate.

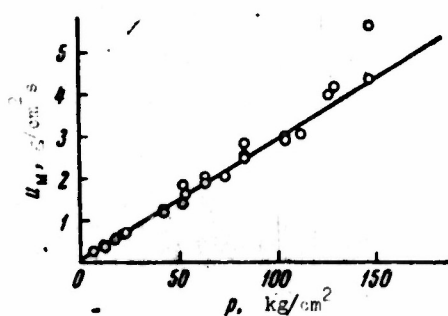


Fig. 101. Dependence of the rate of combustion of 3% gelatin of nitroglycol upon pressure.

The dependence of the rate of combustion of high-molecular nitroester - nitrocellulose - upon pressure in the relatively small interval of low pressures can be expressed by a linear equation [136] but with a considerably larger term A than that for

low-molecular nitroesters. This appears, specifically, in a substantially greater rate of combustion of nitrocellulose at atmospheric pressure in comparison with volatile nitroesters, which are close to it with respect to the heat of combustion. In the wider interval of pressures (up to 150 at) the rate of combustion of nitrocellulose increases not in proportion to the pressure but more slowly (Fig. 102).

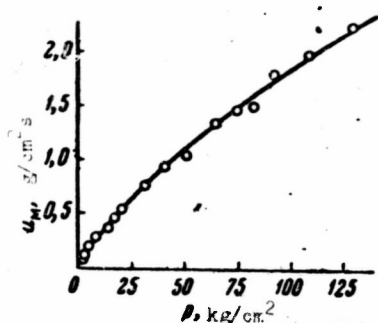


Fig. 102. Dependence of the rate of combustion of nitrocellulose upon pressure.

The comparison of dependences of the rate of combustion of different nitroesters upon pressure reveals some distinctions between them. Thus, if for PETN and nitrolycol¹ this dependence is expressed by a straight line, which passes especially for PETN, practically through the origin of the coordinates, then for nitroglycerine (gelatinized) curve $u(p)$ it has in the beginning a distinctly saturating nature, and only above 30 at can it be approximately expressed by a straight line at a considerable term A in expressions $u = A + Bp$. The rate of combustion of nonvolatile and infusible nitrocellulose in the whole studied interval of pressure - from 150 at - increases according to the saturating curve. The higher the rate of combustion of the nitrocellulose, the higher the nitrogen content.

¹It is interesting that for gelatinized nitroglycol line $u(p)$ at relatively low pressures consists as if it were of two straight lines with a close angle of inclination, and the section for $p < 2$ at is lower than the section which corresponds to pressure above 4 at [137].

The determination of a dependence $u(p)$ during normal combustion was also carried out for 50% gelatin on the base of nitroglycerine and nitroglycol on the strength of the following considerations. The rate of combustion of PETN increases with pressure according to the same simple law both at low and high pressures. This allows assuming that leading complex in the whole range of pressures is the same complex of reactions, and namely, the one which leads the process at low pressures. A comparison of the rate of the combustion of nitroglycerine and nitroglycol makes it possible to verify this assumption. Really, both nitroesters which are very close in composition and thermochemically, burn in atmospheric pressure at considerably (4 times) distinguished rates, obviously, as a result of the difference in kinetics of reactions conducting the combustion.¹ If these reactions retain their leading role at the high pressures, then the difference in the rates should be retained. If at some pressure leading role passes over to final reactions ($\text{NO} + \text{CO} + \text{H}_2 \rightarrow \text{N}_2 + \text{CO}_2 + \text{H}_2\text{O}$), then the rates should become practically identical. It is not possible to compare according to the rates of combustion the liquids directly, since at low pressure a combustion passes over to a disturbed mode. Therefore, it was necessary to use gelatins with high viscosity, although in this case it is possible to fear, that the individuality of liquid nitroesters will be leveled by the large content of nitrocellulose.

Experiments indicated (Fig. 103) which even at 1000 at nitroglycerine gelatin burns considerably faster than nitroglycol gelatin, and hence it can be concluded that the reactions conducting combustion at low pressures play their role down to the indicated pressure.

Belyayev and Komkova [138] studied the combustion of three liquid nitroesters and the solution of nitrobenzene in tetranitromethane

¹At moderately increased pressures the rates of combustion are distinguished less but, nevertheless, considerable.

at increased (10-150 at) pressures of an inert gas (nitrogen). Experiments were conducted in glass beakers with a diameter of 5 and height of 15 mm with the ignition by a Nichrome spiral.

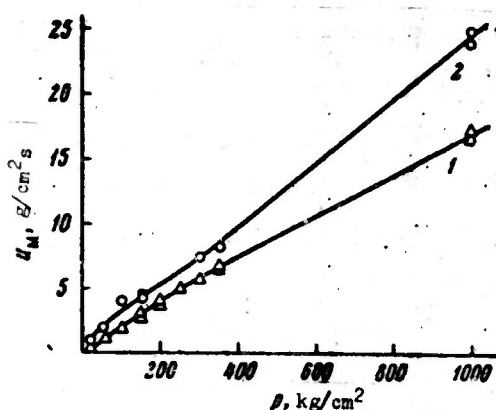


Fig. 103. Dependence of the rate of combustion of nitroglycol (1) and nitroglycerine (2) gelatin upon pressure.

All the studied substances are capable of stable combustion¹ which occurs, however, with a considerably greater rate than it would be possible to expect by extrapolating dependences obtained for a normal combustion at low pressures. This is confirmed by the comparison of the rate of combustion of the liquid and solid² nitroglycerine (Fig. 104) The latter burned 10-20 times more slowly, first of all, because owing to the high viscosity the combustion did not pass over into an accelerated mode, just as in experiments of other investigators in the combustion of gelatinized nitroglycerine.

The dependence of the rate of combustion upon pressure can be expressed by the relationship $u = A + Bp^n$, where for tetranitromethane with nitrobenzene and methyl nitrate $n \approx 1$, and for nitroglycerine and nitroglycol it is somewhat more than 1.

Attention is focused on the considerably higher rate of combustion of the mixture of tetranitromethane with nitrobenzene,

¹In the part of the experiments, especially for nitroglycerine and methyl nitrate, at increased pressures the transition of combustion into an explosion was observed.

²The congealing of nitroglycerine was attained by its cooling in liquid nitrogen. Apparently, investigators obtained in this case not a crystal but supercooled nitroglycerine, which with subsequent test work in a bomb at a room temperature was not possible to be accepted.

although the temperature of its combustion (according to calculations) is only a little higher than that of nitroglycerine. In turn nitroglycerine burns only somewhat faster than nitroglycol, while in a normal mode it burns 4 times faster than does nitroglycol.

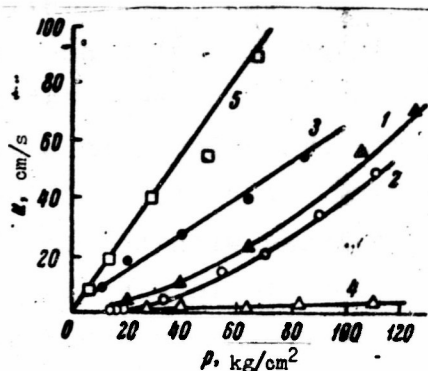


Fig. 104. Dependence of the rate of combustion of nitroglycerine; 2 - nitroglycol; 3 - methyl nitrate; 4 - solid nitroglycerine; 5 - mixture of tetranitromethane with nitrobenzene.

It is known that during the combustion of nitroesters of polyatomic alcohols at atmospheric pressure and moderately increased pressures close to it, a large part of the nitrogen is contained in the products of combustion in the form of an oxide.

Nitric oxide is contained as the basic compound of nitrogen in products of combustion of ethyl nitrate, and in colder products of combustion of propyl nitrate together with the nitric oxides large quantities of nitrites and nitro compounds are contained. At the same time in products of combustion a small quantity of elementary nitrogen is always also contained, and its formation occurs much faster in the front of the flame than in the hotter and reducing atmosphere behind the front.

In the light of these facts, there is an interest in the ability of the nitrites to burn, and the reaction of the dissociation of the nitrites with the formation of the nitric oxide is practically thermally neutral, so that the heat can be liberated only because of the reduction of the nitric oxide. This is referred, specifically, to methyl nitrite, which in vapors (boiling point -18°C) is able to burn even at atmospheric pressure, obviously, because of the

formation in the flames of products which easily reduce the nitric oxides; in the combustion of methyl nitrate this reaction occurs less completely.

The combustion of vapors of methyl nitrite was carried out in two variants [139]. One of them was based on the use of a burner of a flat flame with a diameter of 3.8 cm. The flame was almost invisible, and it was revealed by the shadow method. At various distances from the surface of the burner the chemical composition and temperature of the flames were determined. The gases of combustion were slowly drawn off through a small quartz tube and were frozen in a collector with liquid nitrogen. A gas fraction was analyzed with the chemical and infrared method, the fraction of vapors and liquid - by only the latter method, and water was determined according to the Fischer method. Results of the analyses, in reference to the basic components of products of reaction, are given in Fig. 105. The temperature of the flame was measured by a platinum and platinum-rhodium thermocouple coated by a thin layer of pyrex glass and drawn horizontally in the flame. Curve (1) is shown on the upper figure. The inflection point is the real one, judging by the presence of two sections in the shadow photograph. The rate of combustion with respect to the vapors at 200°C was 7.5 cm/s.

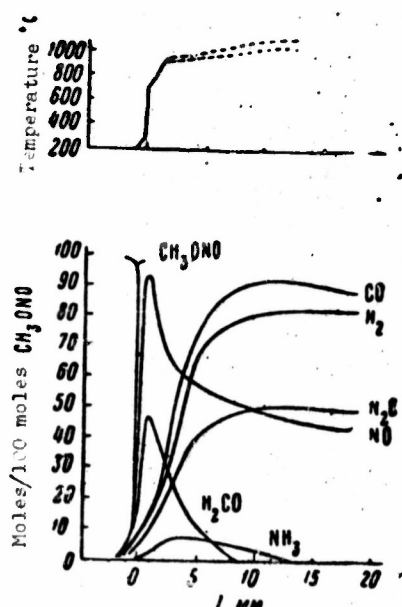
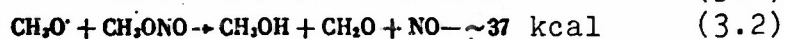
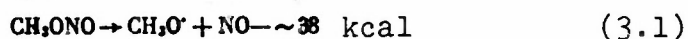


Fig. 105. Distribution of temperature and products in the flame of methyl nitrite.

Described below is the process of combustion on the basis of data themselves. Vapors of methyl nitrite heated up to 160-200°C by the radiation of material of the burner, enter into the zone of the flame and the dissociation, apparently, is completed up to the salient point of the curve of temperature, i.e., up to 700°C. The total equation of the first stage, $\text{CH}_3\text{ONO} \rightarrow \frac{1}{2}\text{CH}_3\text{OH} + \frac{1}{2}\text{CH}_2\text{O} + \text{NO} - 1 \text{ kcal}$ indicates its practical thermoneutrality. Then an exothermal reaction occurs with the formation of water, CO and nitrogen between NO and other products of the indicated reaction or products of their dissociation. This reaction is not continued after the methanol and formaldehyde are decomposed into CO and H_2 , which occurs at a distance of approximately 9 mm from the front of the flame; in this case about half of the NO remains unreduced in end products at a temperature of $\sim 1100^\circ\text{C}$.

The reaction which uses nitrite can be the following:



Reaction (3.1) is considered as the first stage in thermal dissociation of methyl nitrite, but subsequent reactions between its products have not been finally established. Specifically, in reference to the thermal dissociation Levy rejects reaction (3.2).

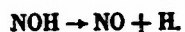
Stacey and Shaw allow the subsequent dissociation metoxyl into formaldehyde and an atom of hydrogen, and the latter with metoxyl forms methyl alcohol. Levy attributes a key role in combustion to reaction



with slow dissociation NOH forms nitrous oxide into water and also alcohol



At the high temperatures of combustion there can become an important reaction



In the second stage reaction, which starts at a distance of 0.5 mm from the front, the following basic compounds take part: NO (42% in volume), CH_3OH (19%) and CH_2O (20%). The exothermal reactions, which sustain the propagation of combustion, should occur between these ingredients, especially as the reduction of NO is ceased, when CH_3OH and CH_2O were used.

It is curious, that during the combustion of isopropyl nitrite, where all three of these ingredients are present approximately in the same relationship, a considerable reduction of NO does not occur. The distinction between both systems consists, in the first place, in the fact that in the flame of the isopropyl nitrate other numerous ingredients are contained, and, in the second place, that the maximum temperature constitutes a total of about 450°C , so that CH_3OH and CH_2O do not compose too rapidly. The most probable explanation consists in the fact that the active product, which is formed of the system of $\text{CH}_3\text{OH}/\text{CH}_2\text{O}$ and reacts with NO, interacts easier with other substances which are contained in the isopropyl nitrate flame, or this product is not formed rapidly enough at 450°C . It is possible that this product is atomic hydrogen, which is formed during high-temperature dissociation of CH_3OH or CH_2O .

During the explosion of vapors of methyl nitrite at atmospheric pressure an addition of NO to nitrite increases the force of the explosion. This was difficult to expect if one considers that in end products of the combustion of nitrite about 50% NO remains unreduced.

In exactly the same manner the lower concentration limit of the mixture with respect to the content of methyl nitrite is very

small - 17.6% (in volume), while in a mixture with nitrogen it is 42.8%.

The dilution of methyl nitrite with a fourfold volume of NO does not lead to products of complete oxidation. A large part of NO remains unchanged and, is formed less than CO and CO₂, but CO remains the main ingredient of the products of combustion; despite the excess of the oxidizer the quantity of N₂O greatly increases, metoxyl, which is especially substantial if it is formed, is then very small; the quantity of CH₂O is changed little.

The possible explanation of the effect of NO is reaction (3.3).

Under conditions in which methyl nitrite is easily ignited and burns, it was impossible to inflame the mixture of two moles of NO, a mole of CH₃OH and a mole CH₂O; it is all the more interesting that methyl nitrite, in the first stage is decomposed into these parts and, moreover, thermally neutral. From results of experiments with vapors of methyl nitrite, diluted by nitric oxides, one should conclude that NO reacts with early formed intermediate products of dissociation of methyl nitrite, which otherwise would react rapidly with the very methyl nitrite. The most probable of them are CH₃O or H especially because the addition of NO inhibits the formation of methanol.

In another work [140] the combustion of methyl nitrite was conducted in air in a vertical glass tube with a diameter of several centimeters. In this case a grayish yellow diffusion flame is formed. On the internal surface of the diffusion flame in the form of a cone on the end of a tube a reddish orange zone is formed. If we decrease the rate of outflow of the vapors, then this weak reddish orange flame is separated from the external diffusion flames and slowly descends in the tube in the form of a flat disc with a weak conical afterglow located over it of the same color easily

visible in darkness. Above this flame on walls of the tube there is deposited a white thin coating, which greatly smells like formaldehyde. The flame of dissociation of methyl nitrite is propagated in a pyrex tube with a diameter a total of 0.7 cm. Apparently, it is capable of being propagated even with smaller diameters (0.65 and 0.53 cm), although under these conditions it is not visible even in darkness.

The rate of combustion very weakly increases with an increase in the diameter of the tube from 1 to 6 cm and at 18°C is about 3.2 cm/s. Despite such a small rate the critical diameter is small. Product *ud* altogether is $\sim 3 \text{ cm}^2/\text{s}$, while for the mixtures of hydrocarbons with the nitric oxides it is equal to $\sim 30 \text{ cm}^2/\text{s}$, and for mixtures hydrocarbon-oxygen-inert gas, $\sim 12 \text{ cm}^2/\text{s}$, possible, because during the combustion of methyl nitrite a reaction uncommon for other mixtures occurring at a considerable rate at relatively low temperatures is carried out.

The linear rate of combustion of methyl nitrite increases with an increase in the initial temperature (Fig. 106), the mass rate of combustion in this case remains approximately constant; at 240°C and higher combustion is not observed. With an approximation measurement by a bare thermoelectric couple, the temperature of the flame was equal to 1100°C; the rated temperature (with respect to the composition of the products of combustion) was 1080°C. The composition of the products of combustion are given in Table 18; given in the third column of the table is the composition corrected for bringing into conformity with stoichiometry.

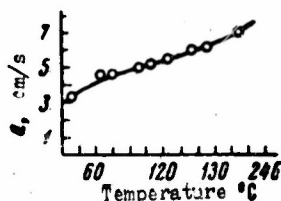
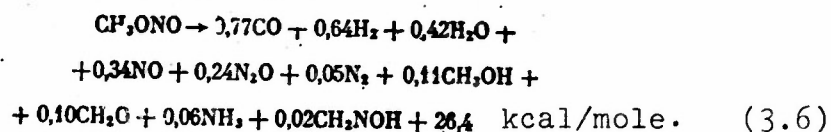


Fig. 106. The change in the rate of combustion of methyl nitrite with a temperature in a tube with a diameter of 2.56 mm. The rate of combustion was measured with respect to hot unburned gas.

Table 18. Composition of products of combustion of methyl nitrite (in moles per 100 moles of burnt methyl nitrite).

Product	Moles found experimentally	Composition corrected for bringing into conformity with stoichiometry	Product	Moles found experimentally	Composition corrected for bringing into conformity with stoichiometry
CO	84	77	CH₃NO N ₂	1,5	1,5
H ₂	59	64	CH ₂ O	1	1
H ₂ O	51	51	Balance with respect to elements		
NO	35	34			
N ₂ O	28	24	C	107	100
CH ₃ OH	11	11	H	289	300
N ₂	5	5	O	210	200
CH ₃ NOH	2	2	N	105	100

Corresponding to this composition is the equation of combustion



The spectroscopic analysis of the flame (with the addition of a small quantity of oxygen for its intensification) indicates that pyrolysis passes basically up to the formation of the flame and nitric oxide, which only partially reacts in this zone is formed.

The absence of combustion with preliminary preheating up to 240°C and above is very interesting. Apparently, the reason of this is the formation of products which are not in a state to take part in self-sustaining reactions in the flame or can even hamper them. The time of stay of the methyl nitrite in heating tube is about 7 seconds, and 2-3% of the decomposition at 240° can take place in this case, which proves to be sufficient in order to make combustion impossible.

It is possible that connected with this is the absence of the effect of initial temperature (at its smaller values) on the mass rate of combustion. The natural increase in the rate at the increase

in temperature is compensated by its decrease, which above 240°C makes combustion impossible.

An attempt to calculate the rate from the equation of Zel'dovich and Frank-Kamenetsiy, on the strength of the assumption that the leading reaction is the same reaction of the first order, which determines the rate of slow dissociation ($E = 36.4$ kcal/mole, $B = 1.84 \cdot 10^{13} \text{ s}^{-1}$), gave $u_z = 120$ cm/s, instead of 3.2 cm/s obtained in an experiment. This fact, along with the distinction of the composition of products of conversion, in both cases leads to the conclusion that the reaction of the initial stage of thermal dissociation is not the determining one during the process of combustion.

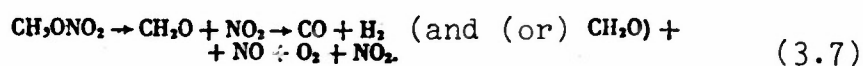
Hall and Wolfhard [141] studied spectroscopically monozonal flames, which were formed during the combustion of some nitrites or mixtures of nitrates, nitrites and nitro compounds with oxygen or air.

It is known that the series of flames sustained by nitric oxides at atmospheric pressure consists of two zones, which are distinguished in color and spectrum and sometimes divided by a nonluminous interval. Such flames are observed during the combustion of hydrocarbons with nitrogen dioxide, and of hydrogen with the mixture of oxygen and nitric oxide. It was established that the first zones are obtained from a reaction between the fuel and NO_2 and fuel and O_2 , respectively, and the second zones are connected with the reaction between the fuel and NO , inasmuch as the last reactions require higher temperature and occur more slowly than the first ones. It was also established that the nitric oxide reacts with respect to one of two ways depending on the chemical nature of the fuel; with hydrocarbons and especially with ammonia the reaction passes at moderate temperatures by a radical mechanism, but in the absence of appropriate radicals, as takes place in flames with H_2 or CO , the nitric oxide sustains the combustion of mixture if the final

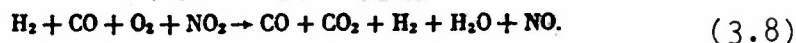
temperature of the flame is quite high for the rapid isolation of the oxygen as a result of the decomposition of nitric oxide.

Taking into account these data and results of spectroscopic analysis of various zones during the combustion of nitrate, nitrite and other mixtures, the authors arrive at the following conclusions relative to the mechanism of the chemical processes in these cases, which occurs in three zones, and the zones of the flame are distinguished in color and spectrum.

For the flame of methyl nitrate without admixtures, one should accept that in the initial first zone a molecule of ester is decomposed, possibly, according to equation



In the second zone



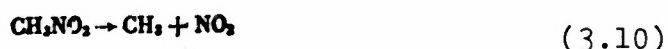
In the third zone H_2 , CO and CH_2O easily react with NO only at temperatures higher than those which are obtained in methyl nitrite flames during combustion under low constant pressures, and therefore the third zone is not observed. It is obtained, however, with explosion in a closed vessel, when a considerably higher temperature is attained.

For a stoichiometric mixture of methyl nitrite with oxygen in the first (blue) zone, a large part of the ester is decomposed into small fragments, formaldehyde and NO ; however, relatively large molecules of supposedly CH_3OH and, possibly, somewhat NO_2 are formed. In the second (orange) weakly expressed zone considerable reactions do not occur. In the third (violet) zone



The organic fuel burns because of the available oxygen and nitrous oxide, if there are any, and then with part of the NO, forming zones CN and NH. The reaction with O₂ precedes the reaction with N₂O and NO.

In the flame of the stoichiometric mixture of nitromethane and oxygen the first zone is absent, and in the second zone there occurs the dissociation



a further oxidation with oxygen and NO₂. In the third zone the organic molecules, which were supposedly formed from initial fragments (CH₃, CH₂, etc.), react with O₂ and then somewhat later in the flame with NO.

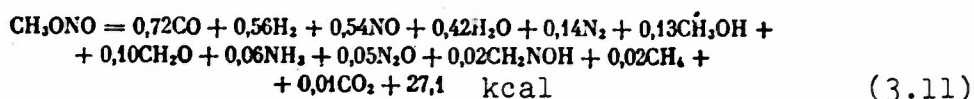
For similar mixture of ethyl nitrate in the first zone the ester is decomposed into NO₂, formaldehyde, acetaldehyde and other organic molecules of close dimensions. In the second zone the partial combustion of the molecules of fuel because of NO₂ occurs, in the third zone oxygen reacts with the organic fuel, and then the latter reacts with NO.

The thermal dissociation of methyl nitrite at a moderately increased temperature forms nitric oxide, methyl alcohol and formaldehyde. This reaction is approximately thermoneutral, and therefore the ability of methyl nitrite to burn was unexpected. The determination of the composition of products of the latter indicated, however, that during combustion part of the nitrogen is reduced to nitrous oxide and even to elementary nitrogen. Ultimately the reaction is exothermal, which makes its ability to self-propagate understandable.

The first stage of chemical conversion during combustion, just as during slow thermal dissociation, is the cleavage of the nitric

oxide. It remained unclear how and why during combustion the transition from the thermoneutral to exothermal reaction occurs, and which of the occurring reactions are the leading ones in this case. For a clarification of these questions the combustion and slow thermal dissociation of vapors of methyl nitrite were studied [142].

The analytic determination of the composition of products of combustion leads to the following equation of conversion:



which corresponds to the temperature of combustion of 1110°C.

With the increase in initial temperature the rate increases (from 3.2 cm/s at 16° to 6.08 cm/s at 180°C). The calculation of the energy of activation according to this data gives 28.5 kcal/mole.

The inert diluents, in decreasing the temperature of combustion and changing the thermal conductivity and coefficient of diffusion, decrease combustion; having the greatest effect is helium, followed by argon and nitrogen. Rated temperatures of combustion agree well with those experimentally measured. Calculation of the energy of activation from that last temperatures gives 32 kcal/mole.

Studied also was the effect on the nature, rate temperature and stability of the flame of impurities of the nitrous oxide, nitric oxides and oxygen (Fig. 107). An admixture of up to 30% (molar) nitric oxide makes the flame brighter, but it does not change its structure. The temperature of combustion in this case rises from 1100° to 1200°C, and the rate increases from 3.2 to 4.3 cm/s. At 30% the nature of the flame is sharply changed. From orange-red monozonal nature it is transformed into a two-zonal with bright blue-biolet internal cone, surrounded by thin red

second zone. The presence of the nitrous oxide even in small quantities, without changing the form and nature of the flame, leads to a great increase in the rate of combustion. The possible reason for this increase is the formation of oxygen with the decomposition of N_2O . With the admixture of the latter the rate of combustion greatly increases.

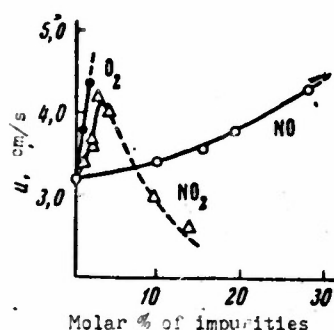
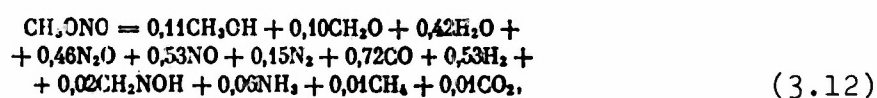


Fig. 107. Effect of impurities on the rate of combustion of methyl nitrite.

The thermal dissociation of methyl nitrite was studied by the flow-through and unlike preceding investigations also at higher temperatures (from 250° to 700°C). At 250° C unlike the "theoretical" equation, which provides the formation of only methanol, formaldehyde and nitrous oxide, noticeable quantities of water and nitrous oxide were obtained. At 700°C the reduction of nitrogen was even more:



according to this, the experimentally determined self-heating with dissociation increased: at 250° it constituted 50°, and at 700-300°C.

The probable reason for the formation of nitrous oxide is the interaction of metoxy radicals with the nitric oxide with the formation of formaldehyde and nitroxyl, giving then the nitrous oxide and water.

Less probable is the formation of nitrous oxide according to the reaction



The nitrous oxide in turn can be reduced to nitrogen by atoms of hydrogen, which are formed during the pyrolysis of methoxyl or formaldehyde.

The question about the leading reaction during combustion remains unclear. The calculation of the rate of combustion under the assumption that the leading reaction is the cleavage of NO gives a rate of combustion equal to 23 cm/s opposed to an experimentally observed rate of 3.2 cm/s. It is possible, therefore, that the initial reaction occurs during combustion at a lower temperature than maximum.

Research on combustion at low pressures [143] has the considerable advantage that the zone of passage of the reaction is greatly expanded in space. This facilitates both the measurement of the temperature profile, and especially the selection of test samples from different parts of the zone.

For ethyl nitrate, for example, at 30 mm Hg, the depth of the zone of combustion is 8 mm, while at atmospheric pressure it is equal to a total of 0.5 mm.

Furthermore, at low pressures various secondary reactions - the reduction of the nitric oxide, the pyrolysis of products of reaction - are absent, and the final temperature is respectively lower.

The feed of vapors of ethyl nitrate was carried out by means of vaporization of the liquid, and they were ignited in the burner with a flat flame. In view of too weak light emission of the front of combustion, its surface was photographed by the schlieren method.

Simultaneously the profile of temperature was measured with the help of a thin thermocouple, and the selection of gases by means of thin (external diameter $d = 0.2$ mm) quartz capillaries was produced.

The depth of the zone of combustion decreases with an increase in pressure and rate of combustion (Fig. 108). In that interval of the pressures (up to 150 mm) where the linear rate of combustion is constant, the depth of the zone of combustion is inversely proportional to the pressure. The rate of combustion was calculated by the division of the volume of burnt gas by the surface of the front of combustion. At an initial temperature of 60°C the rate of combustion is 12.8 cm/s and the final temperature is equal to 786°K .

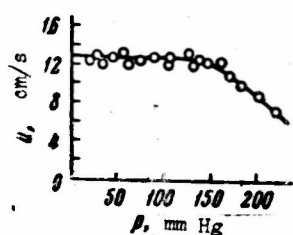


Fig. 108. Dependence of the rate of the flame in vapors of ethyl nitrate upon pressure.

According to the dependence of the rate of combustion upon the final temperature, being changed by dilution with argon, the energy of activation of the leading reaction $E \approx 38$ kcal/mole, which corresponds to the energy of discontinuity of the bond RO-NO_2 was calculated.

The change in the composition and temperature of the gaseous products of combustion in its front is shown in Fig. 109 ($p = 35$ mm, $u = 15$ cm/s, $T = 800^{\circ}\text{K}$). From the obtained dependences and thermal characteristics of the reactive mixture the rates of conductive and convective heat exchange and heat release can be calculated, and, specifically, it is established that more than 50% ethyl nitrate reacts in a zone with a thickness of a total of 2 mm and in the narrow range of temperatures $750\text{--}800^{\circ}\text{K}$.

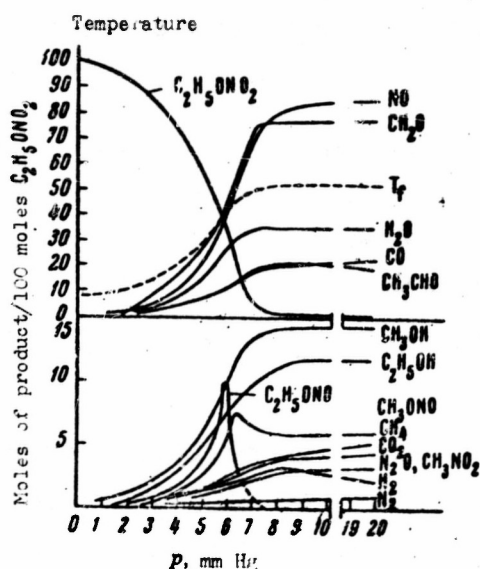
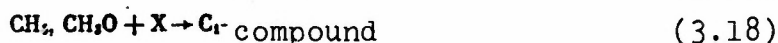
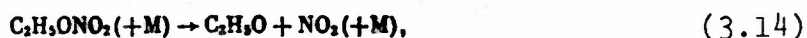


Fig. 109. Profiles of temperature and the composition of products of ethyl nitrate.

One of the intermediate products of combustion is ethyl nitrite. One should note also the formation of about 80 moles of formaldehyde per 100 moles of ethyl nitrate, despite the fact that 1/3 of it was decomposed in a C_2 -compound - acetaldehyde and ethanol. Besides the 5 moles of methane and 2 moles of nitromethane, the remaining carbon is obtained in the form of the compounds, containing the C-O bond. Hence it follows that the bond C-C is broken comparatively easily with a subsequent oxidation. Another substantial fact is the presence in the products of combustion of ethanol, ethyl nitrite, methanol and methyl nitrite, which indicates the participation in the process of combustion of both etoxyl and metoxyl. Inasmuch as ethyl nitrite is one of the basic products of a slow thermal dissociation, it can be concluded that in the low-temperature zone of the flame chemical reactions are similar to those occurring during slow dissociation.

The dissociation of etoxyl, insignificant below 200°C , when during slow dissociation predominately ethanol and acetaldehyde are formed, becomes rapid above 200°C , when among the products formaldehyde and products of reactions of metyl radicals prevail.

Allowing that the metyl radical, being formed in a high-temperature zone, reacts with NO_2 faster, it is possible to accept the following general scheme of combustion of ethyl nitrate at low pressures:



In this scheme M denotes any molecule which, in colliding with a molecule or radical, activates it, and X is the compound capable of reacting with the free radical; these can be both molecules and the free radical itself.

In the low-temperature region compound X for the second type of reactions can be subdivided into those such as NO_2 , which take away the H-atom in etoxyl, and those such as formaldehyde, which give up the H-atom; compounds of the type of nitric oxide react with etoxyl, possibly, with triple collision.

With an increase in temperature in the zone of the flame the ratio $\text{C}_2:\text{C}_1$ decreases as a result of the change in the mechanism of dissociation; apparently, thermal dissociation of the etoxyl radical into formaldehyde and metyl radical occurs; the energy of activation of these reactions (supposedly within limits of 12-34 kcal/mole is more than for the majority of the reactions of the selecting of hydrogen.

The authors assume, that the endothermic disintegration of ethyl nitrate into etoxyl and NO_2 is the leading reaction, which occurs when $p < 150$ mm pseudomolecularly. Subsequent rapid exothermal reactions of alkoxyl and alkyl radicals with the nitrogen dioxide sustain the flame.

2. Hydrazine

Combustion based upon exothermal dissociation of one compound is the simplest of its allowed types. An example of it can be the combustion of hexogen [144], which forms in the dissociation only nitrogen, hydrogen and ammonia. This simplifies the analysis and thermochemical calculations. The kinetics of the initial stage during homogenous dissociation (the breaking of the bond N-N) is also known. Basic are the dependence of the rate of combustion upon pressure $u(p)$, according to which the total order of the reaction can be established, and the dependence of the rate of the reaction upon the temperature $u(t)$, according to which the energy of activation can be calculated.

Combustion was studied both for gaseous hexogen in an enclosed vessel by the schlieren method at the different pressures - up to 10 cm Hg (62°C), and for liquid in narrow tubes at pressures from 10 cm up to atmosphere.

The composition of products of combustion of liquid and vaporous hexogen does not depend on the pressure and closely corresponds to the equation



The change in pressure of 4 times (from 2 to 8 cm Hg) weakly increases the linear rate of combustion of vapors of hydrazine, and this increase, apparently, is conditioned by features of the method. Therefore, one should conclude that the leading reaction is the reaction of the second order. With recalculation for the rate of combustion relative to unburned gas, u_n is equal to 117 cm/s. Diluents (He, Ar, N_2 and NH_3) retard the combustion. Hydrogen and nitrogen, which possess greater heat capacity than argon and helium, lower the rate more greatly. The effect of an inert gas is determined, in the first place, by the lowering of the temperature of combustion and also by the change in thermal conductivity. The rate is more in mixtures with the greater thermal conductivity; for a comparison with

the theory, thermal conductivity was calculated in reference to temperatures attainable during combustion.

In experiments on the combustion of liquid hydrazine critical pressure (the pressure of extinguishment) was measured also, it increased with a decrease in diameter of the tube and also with the dilution of hydrazine by water. The magnitude of the diameter of extinguishment is proportional to the reciprocal of pressure (Fig. 110).

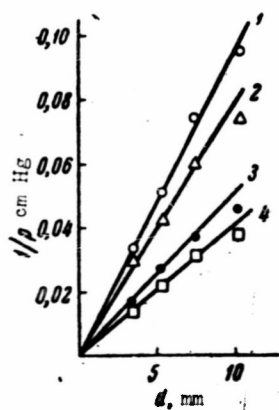


Fig. 110. Pressure of extinguishment for the flame of decomposition of liquid hydrazine. Concentration of N_2H_4 (in %): 1 - 97.7; 2 - 95.9; 3 - 92.7; 4 - 19.4.

At constant pressure the rate of combustion is less in tubes of greater diameter. The region of combustion, depending on the water content, is indicated in Fig. 111, limited by lower and upper pressure limits. The effect the pressure and concentration on this figure are represented in the form of lines of equal rates.

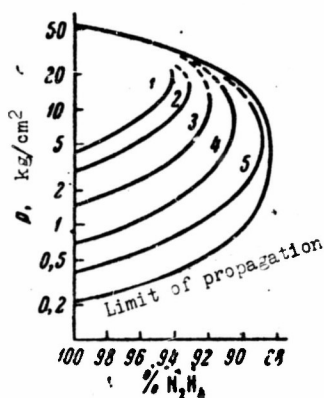


Fig. 111. Limits of stability and the rate of combustion of liquid hydrazine in a tube with a diameter of 5 mm. Results above 1 are taken from work [147]. Rate of combustion (in cm/s): 1 - 0.06; 2 - 0.05; 3 - 0.04; 4 - 0.03; 5 - 0.02.

The rate of combustion, if it is determined in tubes of identical diameter, increases with an increase in pressure, not in proportion to it, but more slowly. It is proposed that this is connected with the heat exchange with the walls of the tube. If the rate of combustion at each pressure is measured, using the diameter of the tube equal to the quintuple value of the critical diameter, then the obtained data indicate (for 97.7% hydrazine) in the interval of pressures 0.5-1 at the direct proportionality of the rate of combustion to pressure. By comparing the dependence of the rate of combustion upon the temperature of combustion, being changed by dilution by inert gases (allowing for the effect of this dilution on thermal conductivity), we obtain the energy of activation equal to 36 kcal/mole. This magnitude, just as that obtained by previous investigators in experiments in combustion (30-45 kcal/mole), is considerably less than the magnitude of the energy of activation of the reaction



($E = 60$ kcal/mole).

Furthermore, in the calculation of rate founded upon this last magnitude, $u = 30$ cm/s instead of 200 cm/s obtained in the experiment.

Thus, the initial reaction of dissociation is not the leading one with combustion.

Antoine [145] studied the combustion of liquid hydrazine in thick-walled pyrex small tubes of different internal diameter (5.6; 9.5 and 12.7 mm) at pressures of 1 to 18 at.

On a graph (Fig. 112) the dependence of $u(p)$ for hydrazine of the concentration of 100, 99 and 97.1% are indicated. In a certain interval of the pressures, the larger the less the diameter

of the tube, the rate of combustion increases with pressure along the saturating curve, then the rate starts to increase linearly and much faster. For hydrazine containing water, the rate of combustion, naturally, is less, and the transition of combustion into a rapid mode approaches at greater pressure.

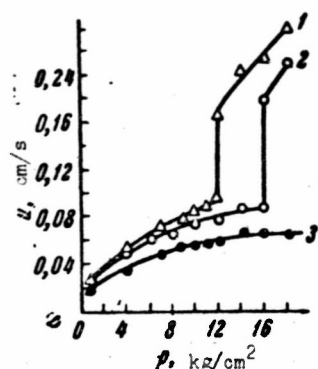


Fig. 112. Effect of dilution on the dependence of the rate of combustion of hydrazine upon pressure. Concentration of N_2H_4 (in %): 1 - 100; 2 - 99; 3 - 97.1.

Studied also was the effect of some other diluents added to the quantity of 1% by volume, which proved to be the action similar to water and increasing in the transition from methyl hydrazine [curve $u(p)$ for which is barely distinguished from the curve for pure hydrazine] to ethyl alcohol, ethylenediamine, n. amylamine, tertiary butyl alcohol, pyridine and n. butyl alcohol.

Attention is given to the great similarity of the indicated dependences with those established for nitroglycol, which is close to hydrazine in absolute value of the rate of combustion; apparently, low rates correspond to the mode of normal combustion and high rates - turbulent; the latter approaches later, at high pressures, the less the rate of combustion and diameter of the tube. The distinction from nitroglycol consists in the fact that the rate of normal combustion is proportional not to the first, but to a considerably smaller degree of pressure. It is possible that this is connected with the fact that normal combustion is carried out, just as the slow thermal dissociation, by the reaction of the first order; the final reaction, which becomes the leading one during combustion in a turbulent mode, a reaction of the second order, in

accordance with which the rate increases in proportion to the pressure.

Murray and Hall [146] determined, by measuring the dimensions of the cone of the flame, the normal rate of combustion of hydrazine,¹ which is decomposed, in accordance with the experimentally confirmed total equation



At an initial temperature of 150° the dissociation according to this equation gives, according to calculation, the temperature of 1660°C; dissociation up to the elements gives a considerably lower temperature ~1100°C. The E , according to Schwartz, is equal to 60 kcal/mole. Determined also was the rate of combustion of the mixtures of vapors with oxygen, which supposedly is carried out in two stages, i.e., initially the mixture of ammonia with nitrogen and hydrogen is formed, and then the hydrogen and ammonia react with the oxygen. By comparing the rate of the combustion of this mixture with the rate of combustion of the artificial mixture ($2\text{NH}_3 + \text{H}_2 + \text{O}_2$), the temperature of the combustion of which according to calculation at 1100°C higher, it is possible to establish the effect of the temperature of combustion on its rate. This can be done also by diluting the hydrazine with water.

The combination of hydrazine has attracted in recent years the attention of investigators [148] for three basic reasons.

On the one hand, hydrazine has a considerable negative heat of formation. Therefore, its dissociation into cells² is exothermic enough that it would be possible to expect its occurrence in the

¹Bamford [147] showed that vapors of hydrazine can explode from a spark or heated body. There are lower and upper limits of pressure; the lower limit of combustion from a spark is 38 mm in a tube with a diameter of 3 cm.

²It is curious that in the combustion of hydrazine in the products there is contained quite a lot of ammonia, in consequence of which the thermal effect of combustion proves to be noticeably more than it would be in the dissociation into the elements.

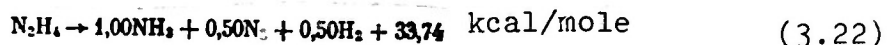
form of a self-propagating process.

In the second place, a molecule of hydrazine contains atoms a total of two elements, and therefore it is natural to expect the simplicity of composition of both the final and intermediate products of dissociation in comparison, for example, with nitrites or the nitrates of polyhydric alcohols. This makes a more convenient object for the comparison of the experimental regularities of combustion with the regularities resulting from various theoretical concepts on this process. Further, hydrazine and some of its derivatives in conjunction with oxidizers obtained recently a considerable application in rocket technology. Finally, the study of combustion the hydrazine itself and systems of hydrazine + + oxidizer can help the clarification of the role of the fuel pyrolysis during the combustion of such systems.

In the analysis of the combustion of hydrazine, being sustained by oxygen, nitrous oxide and nitric oxide, the dissociation of the excess in reagents in non-stoichiometric mixtures was determined and the conditions of the transition with the enrichment of the mixture by fuel from relatively hot flame of oxidation to the flame of decomposition were examined.

The combustion of vapors of hydrazine was studied at 62°C by the schlieren method. In these conditions the rate of combustion is little changed with a change in pressure from 20 to 80 mm Hg. This independence of rate of pressure corresponds to the second order of its leading reaction.

The composition of products of combustion corresponds well to equation



As the calculation indicated, the temperature of combustion

is 1904°K. The linear rate of combustion at 40 mm is 112 cm/s.

The dilution of hydrazine retards the combustion (Fig. 113). A basic role in this case is played by the heat capacity of the diluent, which determines the lowering of the temperature of combustion: nitrogen and hydrogen, which possess greater heat capacity than that of argon and helium, prove to have a powerful effect.

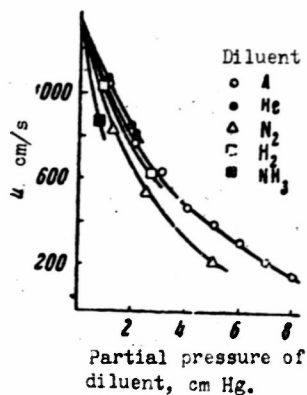


Fig. 113. Effect of diluent on the rate of propagation of the flame (u) into vapors of hydrazine. Pressure of N_2H_4 is 5.02 cm Hg.

Considerable also is the thermal conductivity, the effect of which appears especially evident when the diluent (for example, helium and argon) have identical heat capacity - combustion propagates faster in systems with greater thermal conductivity. The calculation of the energy of activation of the leading reaction gives 35,000 kcal/mole, and according to the temperature dependence of the rate of combustion [146] $E = 3,6500$ kcal/mole.

The rate of the flame in hydrazine-oxygen mixtures (4020 cm/s for a stoichiometric mixture at 40 mm) is considerably more than that of hydrazine itself (1270 cm/s). In mixtures containing more hydrazine, which corresponds to stoichiometry, the magnitude of the increase in pressure indicates that the stoichiometric quantity of hydrazine burns and the excess decomposes; and up to the content of hydrazine of 75% the products of decomposition are hydrogen and nitrogen, and with a greater content of hydrazine the products of combustion contain ammonia also.

For a stoichiometric mixture with the nitrous oxide the rate of the flame at 40 mm is 2400 cm/s (the rate of combustion is 164 cm/s). In mixtures with an excess of hydrazine it decomposes, and with a deficiency in hydrazine the excess of the nitrous oxide decomposes into nitrogen and oxygen.

In mixtures with the nitric oxides the greatest rate of propagation is observed with a certain excess in hydrazine. In the mixtures containing an excess in NO, during chemical analysis its decomposition is detected.

The heat of combustion of mixtures studied is approximately 5 times more than the heat of combustion the hydrazine itself: however, the rate and temperature of the flame are much less distinguished. The main reason is the increase in dissociation of the products of combustion with an increase in its temperature and also the distinction in heat capacity of the products of combustion.

It is interesting that with products of combustion almost identical in temperature and composition of mixtures of hydrazine with nitrous oxide and with nitric oxide (diluted with nitrogen) the rate of the first mixture is 164 and the second only 115 cm/s, which corresponds to a relatively low reactivity of the nitric oxide. However, in conjunction with hydrazine, the nitric oxide, nevertheless, proves to be very reactive in comparison with mixtures where fuel is carbon or hydrogen; a reactivity of NO with respect to the hydrazine is even higher than that with respect to ammonia, possibly, because the nitric oxide easily interacts with the radical NH_2 , being formed in ammonia flame, and, probably, also in mixtures with hydrazine as the base.

In the interpretation of the combustion of mixtures of hydrazine with oxidizers in principle the assumption is possible that the leading dissociation is the dissociation of hydrazine, and the role of subsequent oxidation is limited by an increase in temperature.

However, the gradual increase in the rate of combustion with the addition of oxygen or nitric oxide indicates the opposite of this assumption and in favor of the fact that oxidation in both cases occurs faster than decomposition, although there cannot be considered excluded the possibility of the simultaneous occurrence of both processes, in favor of which spectroscopic observations also indicate. In mixtures with nitrous oxide the relationship of both processes depend on the fuel content.

3. Nitrocompounds and Nitramines

Near atmospheric pressure the rate of the combustion of tetryl and hexogen [149] linearly increases with pressure.

In the interval of the pressures from 1 to 50 at, according to the experiments of M. S. Plyasunov for tetryl and hexogen, pressed in the small plexiglass tubes, the rate increases not in proportion to pressure but more slowly (Fig. 114), and for tetryl it can be expressed by the relation $u_M = 0,065 p^{0.69}$, and for hexogen $u_M = 0,054 p^{0.55}$.

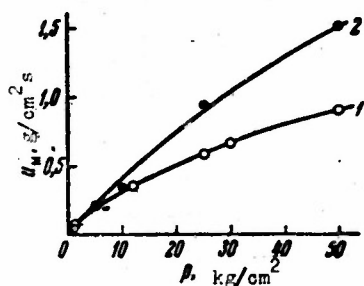


Fig. 114. Dependence of the rate of combustion of tetryl (1) and hexogen (2) upon pressure.

In a wider range of pressure - from 1000 at - the dependence of the rate of combustion upon pressure for trotyl, picric acid, tetryl and hexogen, according to experiments of Glazkova and Tereshkin [118], has the form shown on Fig. 115. For the first two substances this dependence in the whole interval of pressures is linear. For tetryl the curve $u(p)$ up to 250 at has a saturating

nature, and at high pressures the rate increases linearly with pressure, by a linear equation the rate of combustion of hexogen can be approximately expressed in the interval of 100-1000 at. Numerical values of the coefficients of equations are given in Table 19.

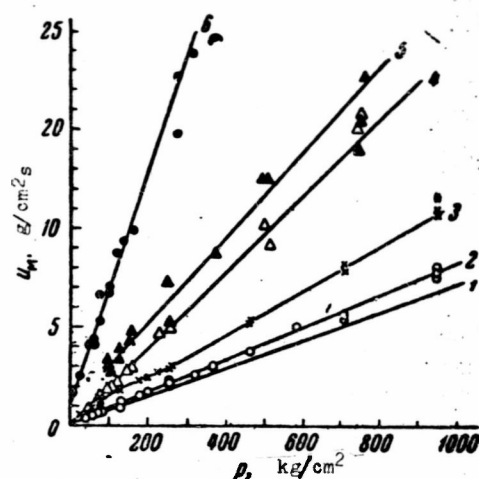


Fig. 115. Dependence of the rate of combustion of trotyl (1), picric acid (2), tetryl (3), PETN (4), hexogen (5) and gelatinized nitroglycerine (6) upon pressure.

Table 19. Values of coefficients A and B in equation $u = A + Bp$ for a number of explosives.

Explosives	Interval of the pressures in which the equation is valid, at	A	B
Trotyl	20-950	0.04	0.00716
Picric acid	25-950	0.14	0.00805
Tetryl*	250-950	0.04	0.0114
Hexogen	100-1000	0.90	0.0216

*In the interval of the pressures 10-250 at $u_H = 0.063 p^{0.696}$.

4. Initiating Explosives

The data given above refer to secondary explosives, i.e., relatively stably burning explosives. Great interest, naturally, was created also by the determination of the dependence $u(p)$ for the initiating explosives especially as the instability of their combustion was supposedly connected with the great magnitude of the

rate of combustion and the effect of pressure on it. However, the instability of combustion complicated the indicated determination - it is possible to fear that initiating explosives are generally incapable of stationary burning and that by such methods, as, for example, the increase in density or decrease in external pressure, is it possible only to decrease the instability and increase the section of combustion up to the initiation of the explosion. Therefore, the first investigations [150] in the indicated direction were conducted with initiating explosives, diluted by inert admixtures or secondary explosives, which decrease the rate of combustion. It was proposed that, having determined the rate of combustion as the function of the diluent content, it will be possible by extrapolation to determine the rate of combustion of a pure initiating explosive.

Experiments were conducted with fulminating mercury and trinitroresorcinate of lead with talc, tetryl and nitrocellulose as diluent. In charges of low density mixtures of fulminating mercury with talc burned unevenly - with a high and greatly oscillating rate, mixtures of trinitroresorcinate of lead with talc or tetryl with small contents of the diluent give a flash or explosion, and at large contents they do not burn. Mixtures of trinitroresocinate with nitrocellulose in the definite interval of composition are capable of combustion and according to the rate, which rapidly increases with the increase in the content of trinitroresorcinate or pressure, exceed the nitrocellulose by several times.

For the first time Belyeyev showed that many of the initiating or quick-burning explosives (fulminating mercury, trinitrotriazidobenzene, cycloacetone peroxide, diazodinitrophenol, potassium picrate) in a greatly condensed state are capable of stationary combustion not only in a vacuum, but also at increased (up to 150 at) pressures [151]. Their rate of combustion was measured at ten and more times exceeding the rate of combustion of the most rapidly burning secondary explosive. Delyayev discovered also the considerable features of the combustion of initiating

explosives - its occurrence with intensive dispersion. This mode of combustion is typical for initiating explosives but is carried out also for secondary explosives under some specific conditions of combustion.

External combustion of the studied initiating explosives appears in the following manner. With the combustion of fulminating mercury under reduced pressure (150 mm), a dark zone of a considerable extent, and a bright flame appears only at a certain distance from the surface. At the pressure below 40-50 mm the flame disappears completely, the disk "melts" without apparent light, and formed on walls of the vessel is a considerable thin coating of soiled fulminating mercury, the quantity of which constitutes not less than $\frac{2}{3}$ of the initial charge. With the combustion of pressed fulminating mercury in a vacuum, the breaking of the disk into small pieces of small magnitude, which either burn or remain unburned sometimes is observed.

In the experiments of P. F. Pokhil combustion of fulminating mercury in a vacuum occurs at a pressure of 10-15 mm and temperature above -20° ; the temperature on the surface of the condensed phase is $270-320^{\circ}\text{C}$. With an increase in pressure a cold-flame combustion is observed, and at 25-30 mm at a considerable distance over the surface of the specimen there appears a flame visible in daylight. The thermal effect of the reaction in a condensed phase is according to calculations of Pokhil, 48-60 cal/g.

The other explosives studied by Belyayev behave at reduced pressures somewhat differently. With the combustion of tricycloacetone peroxide under a pressure of 100 mm on walls of bell jar there is a white thin coating. If this thin coating is gathered and set on fire, then it easily flashes. However, this is not a peroxide but a substance with a higher melting temperature and is less volatile. With the combustion of trinitrotriazidobenzene with a decrease in pressure, the flame in the beginning is weaker and stretched, and then it decreases in size. At 10 mm the flame is very weak and small.

For the determination of the dependence $u(p)$ of fulminating mercury at increased pressures [152] its disks ($d = 4$ mm, $h = 5-6$ mm, relative density, 0.96), coated on the side surface by a layer of shellac or petrolatum jelly, were ignited by a Nichrome wire in the bomb filled with nitrogen. The recording of the combustion was produced with the help of a time magnifier in a weak passing light (Fig. 116) In these conditions of the experiment at atmospheric pressure, or the apparent light emission in the beginning of combustion is not revealed; if the flame appears later, then it is located at a considerable distance from the surface of the disk, and there appears to be no substantial effect on the rate and nature of the combustion. This effect is not observed with increased pressures when the flame approaches the surface of the charge. The dependence of the rate of combustion upon pressure is shown on Fig. 117. With an increase in pressure the increase in the rate is retarded. If earlier [153], on the basis of results of experiments at reduced pressures, it was expressed by the relation $u_n = 0,4 + 1,1 p$, then at increased pressures $u_n = 1 + 1,04 p^{0,5}$.

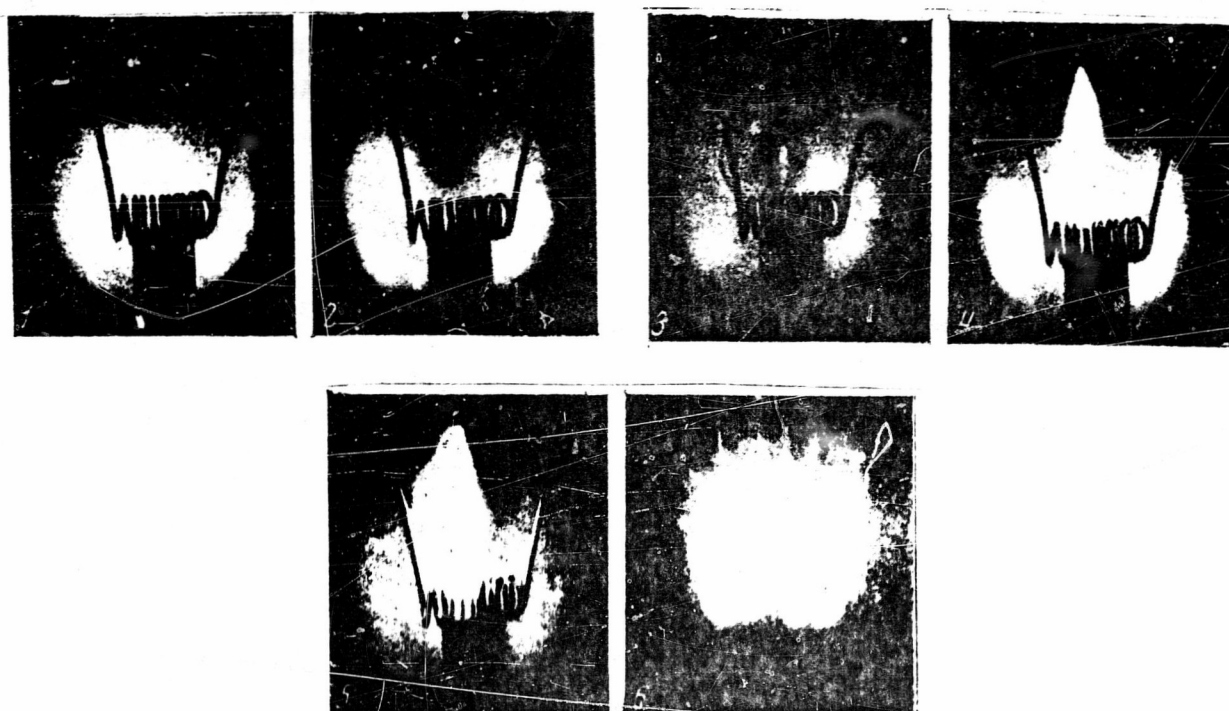


Fig. 116. Photograph of the combustion of fulminating mercury. 1 - disk of fulminating mercury directly before the beginning of combustion; 2 - beginning of a gasification, time, $2 \cdot 10^{-3}$ s; 3 - appearance of a weak light emission, time $4 \cdot 10^{-3}$ s; 4 - appearance of flame on the spiral time, $6 \cdot 10^{-3}$ s; 5 - passage of flame into spiral, time, $14 \cdot 10^{-3}$ s; 6 - spiral-moved to the side, burned $1/3$ of the disk, time, $130 \cdot 10^{-3}$ s

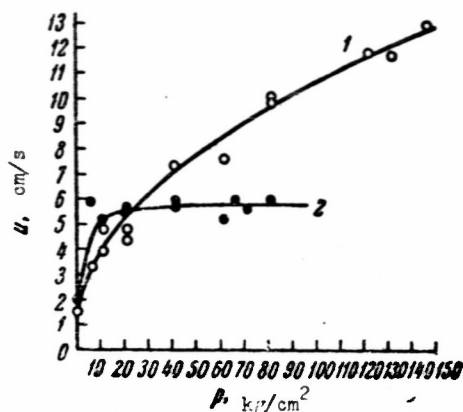


Fig. 117. Dependence of the rate of combustion of fulminating mercury (1) and potassium picrate (2) upon pressure.

Up to even high pressures (1000 at) the rate of combustion of fulminating mercury (containing 5% paraffin) was determined by S. V. Chuyko. At a relative density of 0.95-0.99 combustion in small plexiglass tubes occurred in the majority of experiments evenly and without transition into an explosion. The rate of combustion is great; it grew with pressure along the saturating curve and reached $18 \text{ g/cm}^2\text{s}$ at 400 at.

Belyayev [154] also determined the rate of combustion of pressed mixtures of some initiating or quick-burning substances depending on the relationship of the components. An admixture to fulminating mercury of a total of 2% lead azide leads to detonation upon ignition. At the temperature of liquid nitrogen the mixtures burn up to a content of 15% azide, and the rate of combustion considerably increases with an increase in the content of the latter (Fig. 118). The rate and stability of combustion greatly depend on the nature of the restrictor of the side surface of the charge. If instead of petrolatum jelly there is used a thin layer of collodion, then the rate of combustion becomes considerably more, and at a smaller content of azide it turns into an explosion.

The rate of combustion of a mixture of relative slowly burning (0.70 cm/s) trinitrotriazidobenzene with more rapidly burning fulminating mercury (1.6 cm/s) increases with an increase in

content of the latter in the beginning slowly, and then, starting from 70% fulminating mercury, more rapidly (Fig. 119).

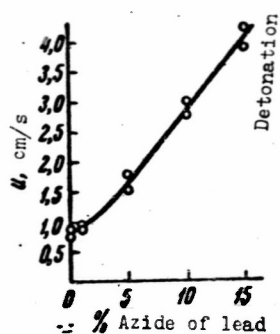


Fig. 118. Rate of the combustion of mixtures of lead azide with fulminating mercury at the temperature of liquid nitrogen.

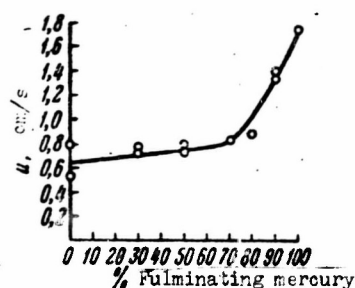


Fig. 119. Rate of combustion of mixtures of fulminating mercury with trinitrotriazidobenzene.

The rate of combustion of trinitrotriazidobenzene with trinitroresorcinate of lead (Fig. 120) also increases with an increase in content more rapidly than the burning component; just as in the preceding case, an increase occurs in the beginning slowly and then much more rapid. The characteristic of this mixture is its incapacity of a stable combustion in a certain (30-40%) interval of the content of trinitroresorcinate - with ignition combustion appears, but it occurs unevenly, as if by individual shocks, and upon the stopping of the action of the igniter it is extinguished.

Belyayev and Kondrashkov studied the combustion of potassium picrate at increased (up to 125 at) constant pressures [155]. Svetlov and Fogel'zang determined the dependence of the rate of combustion upon the pressure (up to 400 at) of picrates of a number of metals - lithium, sodium, potassium, rubidium, beryllium, magnesium, barium,

zinc, silver, lead and iron (bivalent and trivalent), potassium trinitrobenzoate and also some styphnates, specifically, lead [156]. Experiments were conducted with small cylinders of a substance in the bomb of constant pressure in an atmosphere of nitrogen, which are pressed up to a density of 0.9-0.95, lacquered on the side surface or by the pressed in small plexiglass tubes.

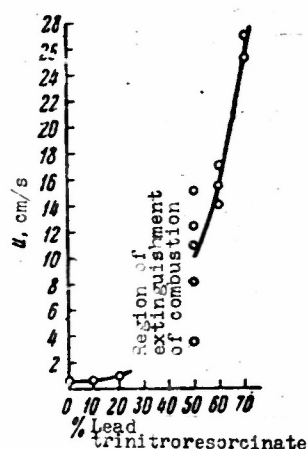


Fig. 120. Rate of combustion of mixtures of trinitroresorcinate of lead with trinitrotriazidobenzene.

The rate of combustion of potassium picrates (just as the majority of other picrates) at atmospheric pressure is small (0.40 cm/s), but increases very rapidly with pressure, passes at 8 at through a maximum (7 cm/s), decreases at 80 at to a minimum (2.50 cm/s) and then again but slowly increases, reaching at 350 at 5 cm/s (Fig. 121).

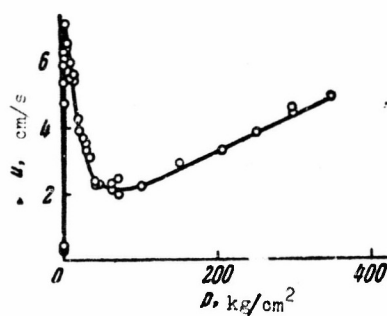


Fig. 121. Dependence of the rate of combustion of potassium picrate upon pressure.

The curve of the dependence of the rate of combustion upon pressure for some of the studied picrates and styphnates of the

same type as that for potassium picrates; for the others it is substantially different, approximating the type of curves characteristic for fulminating mercury or lead picrates. Various picrates are greatly distinguished in magnitude of the rate at increased pressures, which changes from 3 to 30 cm/s.

It was possible to obtain the stable combustion of the most rapidly burning of the studied substances - lead styphnate. In the thick-walled (2 mm) small plexiglass tubes of small diameter the lead styphnate burned stably in the whole studied range of external pressure - from 15 mm Hg to 400 at. The rate of combustion is very great (25-26 cm/s) in a vacuum, weakly increases with an increase in pressure up to 50 at, and then - up to 400 at - remains almost constant (Fig. 122). According to the nature of the curve $u(p)$ lead styphnate is similar to lead picrate. The latter is distinguished, however, by the inability to burn in given conditions of an experiment at pressures below 20 at. At the same pressure (18 at), starting from which the lead picrate acquires this ability, the rate of its combustion is almost 30 times less than that of styphnate, but it rapidly increases with pressure and above 200 at is only 10-15% less than the rate of combustion of styphnate.

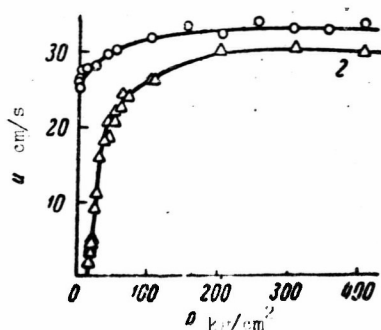


Fig. 122. Dependence of the rate of combustion of lead styphnate (1) and lead picrate (2) upon pressure.

B. S. Svetlov and A. Ye. Fogel'zang in their experiments detected the unique effect of the shell of the charge of a rapidly burning explosive on its combustion. Thus, with lead picrate in tubes with an internal diameter of 7 mm and thickness of the walls

of 1 mm at pressures above 30 at there occurred explosions, possibly, because of the inadequate strength of the tube, which was expanded during combustion; in this case the formation of a slit, where gases could penetrate is possible. The expansion of the wall up to 2 mm with the simultaneous decrease in the internal diameter down to 4 mm removed the initiation of explosions.

Further it was detected that if the end is located near the shear of the tube of the charge does not have a durable shell but is only lacquered on the side, when the rate of combustion is considerably (approximately 4 times) more than that when it is deep into the tube. Correspondingly, with a charge wholly filling the tube, the rate of combustion decreases as it departs into the depth of the tube, reaching at the depth of the free section 2-4 mm of constant magnitude.

This is explained, specifically, by the distinction of absolute values of the rate of combustion of potassium picrate, obtained by B. S. Svetlov and A. F. Belyayev; the latter carried out experiments with charges armored by means of the lacquering of the side surface, which, respectively burned faster than cartridges deepened into plexiglass tubes in experiments of Svetlov and Fogel'zang. Let us add that the general nature of the dependence $u(p)$ is retained, although some quantitative distinctions are observed (Fig. 123).

The interesting effect of cubic density on the stability of the normal combustion of potassium picrate was detected by V. V. Gorbunov. At atmospheric pressure picrate of bulk density ($\sim 1 \text{ g/cm}^3$) burned at the usual rate, and picrate of increased density ($\sim 1.2 \text{ g/cm}^3$), i.e., less gas permeability, burned in conditions of an accelerated mode at the rate of 3 times greater.

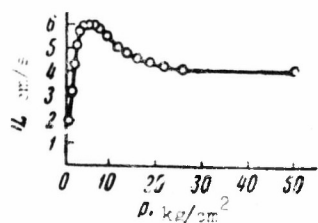


Fig. 123. Dependence of the rate of combustion of potassium picrate (small cylinders with a diameter of 4 mm coated on the side surface with lacquer) upon pressure according to the data of Belyayev [155].

The effect of some admixtures on the combustion of potassium picrate was studied also; picric acid with a content of 20% 2-3 times retards combustion at atmospheric pressure considerably less than at 5-50 at, and at 125 at the rates of combustion are practically identical. The mixture of potassium picrate with perchlorate (1:1) does not indicate the maximum of the rate. Potassium bisulfate, according to Svetlov and Fogel'zang, lower the rate combustion in the interval of pressures from 1 to 30 at and increases it at high pressures (Fig. 124); the maximum of the rate is somewhat displaced to the side of the lower pressures. The presence of ammonium carbonate acts similarly (Fig. 125), but the uniformity and stability of combustion are greatly decreased.

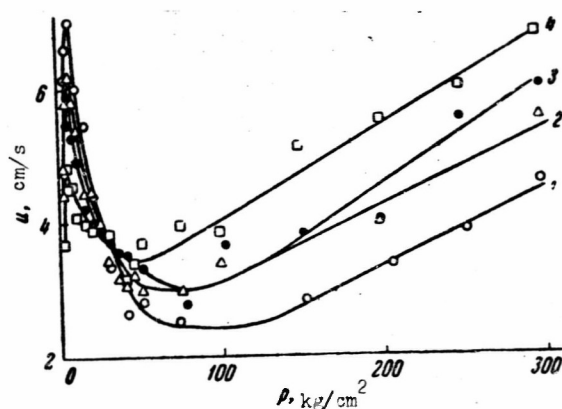


Fig. 124. The effect of potassium bisulfate on the rate of combustion of potassium picrate. 1 - potassium picrate; 2 - 10% potassium sulfate; 3 - 20%; 4 - 30%.

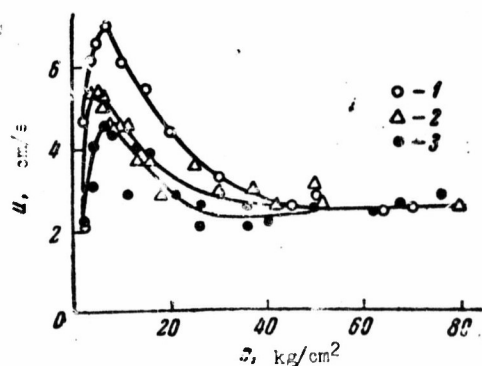


Fig. 125. The effect of ammonium on the rate of the combustion of potassium picrates. 1 - potassium picrates; 2 - 10%; 3 - 20% $(\text{NH}_4)_2\text{CO}_3$.

A. Ye. Fogel'zang also studied the combustion of salts of dinitrophenol (lithium, potassium, lead), ortho- and paramononitrophenol (potassium and lead) and mononitroresorcin (potassium and lead). The majority of the salts studied possesses much the greater capacity¹ and rate of combustion than it would be possible magnitude of the heat of combustion, which because of the great deficiency in oxygen is much less than that, for example, of trinitro compounds of the same phenols. Apparently, this is connected with the fact that reactions during the combustion of salts (unlike polinitrophenols) pass up to the end with complete thermal effect; it is possible that here the catalytic action of metal plays a role. The most widespread type of combustion - the rapid increase in the rate at low pressures and greatly retarded at moderately increased pressures; as an example Fig. 126 gives a curve for lead dinitrophenol. For potassium salts the dependence with a maximum is observed (similar to potassium picrates). Potassium salts of ortho- and paranitrophenol are greatly distinguished according to their ability to burn.

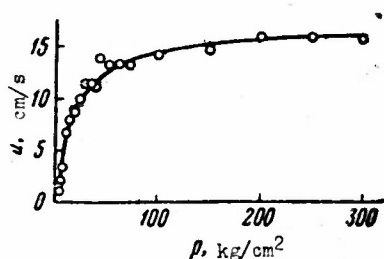


Fig. 126. Dependence of the rate of combustion of lead dinitrophenolate upon pressure.

A. Ye. Fogel'zang also studied the combustion of barium azide (Fig. 127), which occurs with respect to dependence $u(p)$ similar to that of fulminating mercury but with considerably smaller rates.

The low capacity of combustion is characterized also by calcium azide [157], despite the fact that the rate of its combustion in those few experiments in which it took place was relatively great

¹Specifically, di- and mononitrophenolate of lead start to burn at much lower pressures than does trinitrophenolate.

(0.5-0.7 g/cm²s at atmospheric pressure). The combustion is accompanied by an intense dispersion of an unburned substance. At increased pressures the calcium azide is capable of stable combustion; at 21 at the rate of combustion was 4 g/cm²s.

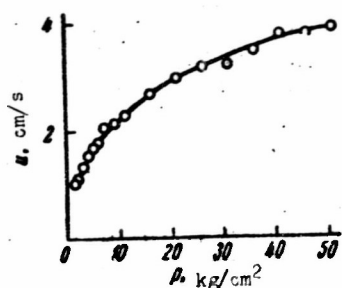


Fig. 127. Dependence of the rate of combustion of barium azide upon pressure.

5. Ammonium Perchlorates and Nitrates and Mixtures with Them as the Base

Perchloric acid is a more active oxidizer than that of nitric acid. This distinction is retained in ammonium salts. The capacity for the combustion of perchlorates capable of intramolecular oxidation is considerably more than that of nitrates. This allowed studying the dependence $u(p)$ for the ammonium perchlorate without organic additions.

In a bomb of constant pressure filled with nitrogen at pressures up to 1000 at, the combustion of ammonium perchlorate was studied by Glazkova [130]. Small cylinders of salt, pressed up to a density of close to the specific weight in a shell or without it were ignited on upper end by an incandescent wire; the rate was measured by a photographic recorder.

Dependence $u(p)$ is unique (see Fig. 93) and is partly similar to that observed for the potassium picrate; it includes the section of the drop in rate with an increase in pressure; in the range of the pressures of 500-1000 at curve $u(p)$ is convex to the axis of the abscissa.

In order to explain to what degree the indicated dependence is characteristic for perchlorate and to what degree it depends on incidental effects, experiments at the different pressures were conducted under various conditions. Experiments with various diameters of the charge (5, 7 and 10 mm), represented in Fig. 93, indicate that in the interval of the pressures up to 400 at the rate of combustion does not depend on the diameter. This indicates that the values of the rate are not distorted by the effect of heat losses. Inasmuch as products of combustion of perchlorate possess oxidizing properties and the material of the shell which was used in the experiments (plexiglass) is ignitable, their interaction in principle could affect the rate of propagation of the process. In order to establish the

reality of this effect, there were used different shells - Plexiglass tube and a thin (0.1 mm) tube of perchlorvinyl lacquer; in the latter case at pressures above 150 at (Fig. 128) the rate is noticeably more; however, it is more in the case of the stoichiometric mixture of perchlorate with fine-grained Plexiglass, where it is difficult to assume a chemical interaction with the shell. The reason for the distinction in rates in different shells in both cases remains unclear.

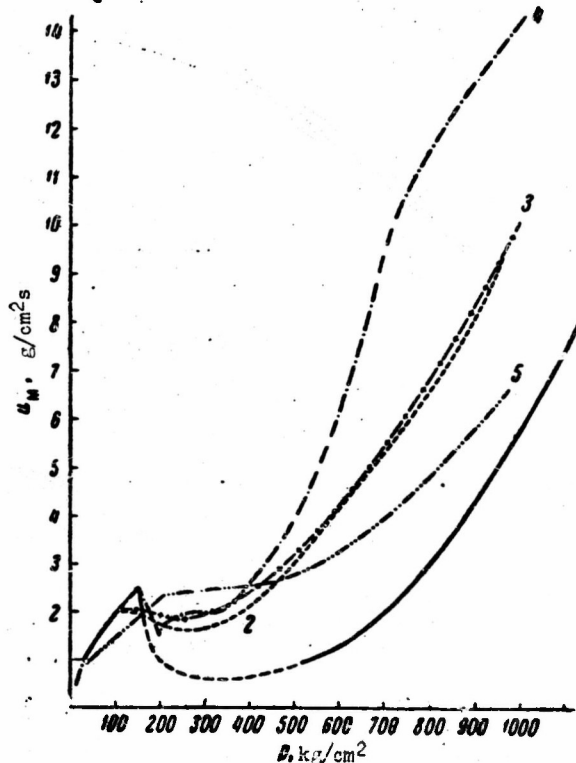


Fig. 128. Dependence of the rate of combustion of specimens of ammonium perchlorate in various shells upon pressure. 1 - without a shell; 2 - in perchlorvinyl lacquer (0.1 mm); 3 - in a tube of perchlorvinyl lacquer (1 mm); 4 - in Plexiglass tubes; 5 - in a fluorinated lubricant. On curved 1 the dashed line denotes the region of pulsating combustion.

The change in the thickness of the layer of perchlorvinyl lacquer from 0.1 to 1 mm did not change the general nature of the dependence $u(p)$ and in the range of the pressures up to 200 at - even and the magnitude of the rate.

If at pressures up to 400 at the effect of the shell on the rate of a combustion proves to be slight, then at 500-1000 at it becomes considerable (see Fig. 128). The greatest rate of combustion at 1000 at ($14 \text{ g/cm}^2\text{s}$) is indicated by perchlorate in a plexiglass shell with a thickness of 1 mm, and it burns considerably more slowly in thin (0.1 mm) tubes of perchlorvinyl and even more slowly in the form of bare small cylinders or small cylinders coated with a thin layer of fluorinated lubricant.

In order to explain, whether or not these distinctions are connected with the effect of heat losses, experiments in a thin perchlorvinyl shell were conducted (at 1000 at) with various diameters; with the increase in diameter from 3 to 10 mm the rate of combustion increased from 8.3 to $10.0 \text{ g/cm}^2\text{s}$ too little in order to explain all the observed distinctions. Moreover, with the combustion of small bare cylinders of perchlorate the rate of combustion with small diameters (3 and 7 mm) was noticeably more ($7.5 \text{ g/cm}^2\text{s}$) than that with a diameter of 15 mm ($6.0 \text{ g/cm}^2\text{s}$), in contrast to that which could be expected if the distinction was determined only by relative heat losses.

Furthermore, at large diameters (15 mm) the rate of combustion of bare charges is almost twice less than that with charges in a thin perchlorvinyl shell. Apparently, effective in the combustion of ammonium perchlorate are some factors not playing a substantial role in the combustion of other earlier studied explosives, which are perhaps similar to those which appear (specifically, with respect to the effect of the shell) for potassium picrate. Apparently, at high pressures combustion in plexiglass tubes is determined by the interaction of perchlorate with the walls of the tube, and more weakly expressed in the combustion of perchlorate in a perchlorvinyl shell. The mixtures of perchlorate with paraffin in both shells (and also without a shell) give similar rates.

The rate of combustion and the nature of the curved $u(p)$ of ammonium perchlorate are greatly changed in the presence of catalytic agents (Fig. 129) (let us stipulate that the experiments were conducted in small plexiglass tubes). Potassium bichromate also accelerates the combustion of mixture of perchlorate with coke (Fig. 130).

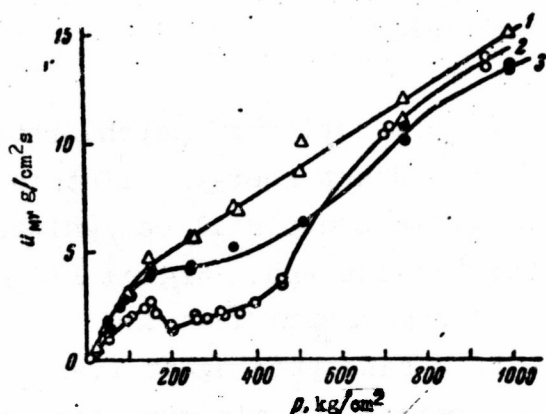


Fig. 129. Effect of catalytic additions (5%) on the rate of the combustion of the ammonium perchlorate. 1 - with potassium bichromate; 2 - pure perchlorate; 3 - with chromic oxide (Cr_2O_3).

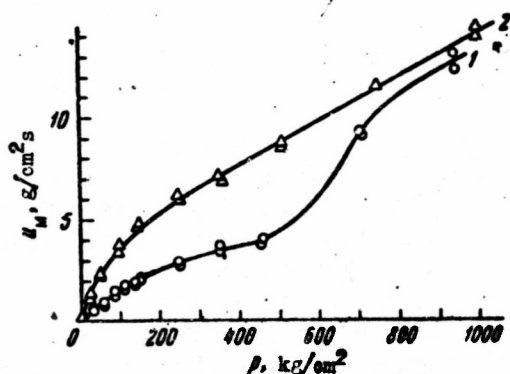


Fig. 130. Effect of potassium bichromate (5%) on the rate of combustion of the stoichiometric mixture of ammonium perchlorate with coke. 1 - pure mixture; 2 - mixture with potassium bichromate.

The stoichiometric mixtures of perchlorate with some fuels (paraffin, coke, saccharase) [158] were also studied (Fig. 131). The mixtures with coke and saccharase in the region of the low pressures, just as Plexiglass mixtures, burn more slowly than does

the perchlorate itself, although their ability to burn, being characterized by critical pressure, is considerably higher. This indicates the fact that a leading role in combustion under these conditions is played by the chemical conversion of perchlorate; the interaction of its products with the fuel occurs too far from the surface of combustion in order to affect the rate of its movement. On the whole the dependence $u(p)$ has a complex nature. The heat of combustion of the mixture by itself does not prove to be the determining effect on the magnitude of the rate of combustion and to its dependence on pressure.

Levy and Friedman [131] studied the combustion of perchlorate with constant feed to the burning end of radiant energy. If this feed is not less than $10 \text{ cal/cm}^2\text{s}$, the perchlorate will be ignited in several seconds and continues to burn to the end. Figure 132 shows the dependence of the rate of such combustion upon the intensity of radiation. The presence of a catalytic agent greatly increases the rate of combustion and decreases the minimum intensity of the light flow necessary to obtain combustion. The slope of straight lines is, apparently, affected by the change in the coefficient of absorption of the surface of perchlorate in the presence of a black catalytic agent.

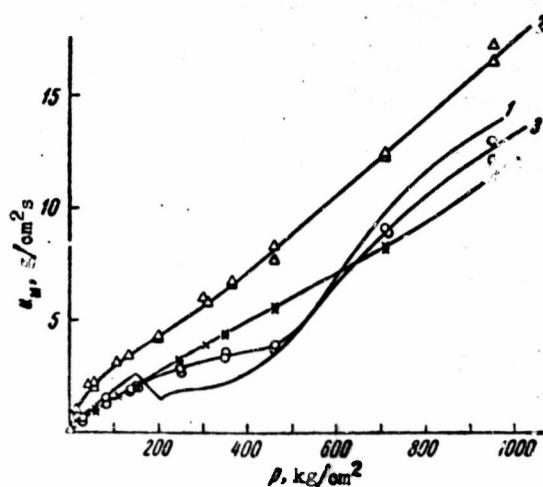


Fig. 131. Dependence of the rate of combustion of some stoichiometric mixtures of the ammonium perchlorate with fuels on pressure. 1 - ammonium perchlorate; 2 - mixture with paraffin; 3 - with coke; 4 - with saccharase.

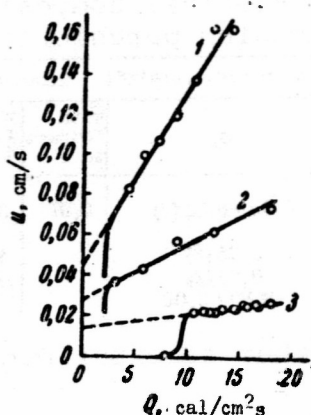


Fig. 132. Effect of the intensity of radiation on the rate of combustion of pure and catalyzed perchlorate ammonium. 1 - 3.0% copper chromite; 2 - 0.5% copper chromite; 3 - NH_4ClO_4 without additions.

Investigators determined also the composition of gas products of the combustion of perchlorate at various pressures in order to obtain the concept on the sequence of reactions occurring here. At increased pressures gaseous products consisted of nitrogen, of nitric oxide and oxygen. The water which was in the container for combustion contained a nitrate ion and also ions of ammonium and perchlorate in small equivalent quantities; the latter, obviously, were obtained on account of the fact that part of the perchlorate avoided combustion, possibly, as a result of dispersion. The absence of a nitrite ion is explained by the fact that the nitric oxide formed during combustion reacted with the oxygen (which, moreover, was more) more rapidly than that with chlorine. Nitrous acid formed with the interaction of NO_2 with water in the presence of water was oxidized by chlorine up to nitric acid. At atmospheric pressure the composition of the products was somewhat different, but this was partly explained by the fact that conditions of the selection of samples were different than those at increased pressures.

The effect of pressure on the relationship between the individual composite parts of products of combustion is indicated on Table 20.

Table 20. Effect of pressure on the chemical composition of products of combustion of ammonium perchlorate.

Pressure, at	Quantit. of moles of gas per mole of burned ammonium perchlorate*				Balance	
	NO ₂	N ₂ O	N ₂	O ₂	with respect to N	with respect to O**
Atmospheric	0,55±0,02 (5)	0,10±0,01 (2)	0,11±0,01 (2)	0,65±0,02 (2)	0,97	3,25
35	0,31±0,01 (5)	0,11 (1)		0,75 (1)		4,23
70	0,23±0,01 (12)	0,12±0,01 (2)		0,80 (2)		4,18
140	0,23±0,01 (3)	0,05 (2)		0,80±0,04		4,11

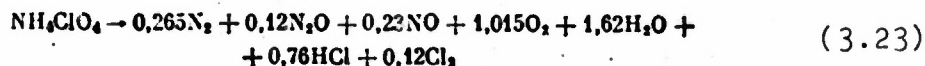
*Numbers in parentheses - the number of experiments whose results are averaged.

**The assumption was made about the fact that for a mole of burned ammonium perchlorate 2 moles of water are formed. In the calculation of balance with respect to oxygen in experiments at atmospheric pressure one of two atoms of oxygen in NO₂ is obtained from reactions with water, so that only one of the oxygens is calculated in the balance. At higher pressures the second oxygen in the nitrogen dioxide is taken from products of combustion, and gaseous oxygen and both oxygens in the nitrogen dioxide are respectively calculated.

The portion of nitrogen oxidized to an oxide depends upon the pressure, decreasing from 0.55 at atmospheric pressure down to 0.23 at 70 at and then, apparently, remained constant: the yield of nitrous oxide does not depend on the pressure up to 70 at but drops with its increase up to 140 at. The presence of a catalytic agent (at 70 at) greatly decreases the content of the nitrous oxide.

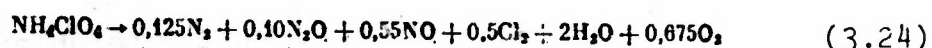
The same effect, although to a lesser degree, proves to be the increase in the cross section of the specimens.

In the calculation of the temperature of combustion (for 70 at), based on the experimentally steadied relationship of nitrogen compounds (N₂:NO:N₂O = 1:0,87:0,45) and the assumption that hydrogen chloride, chlorine, water and oxygen are in thermodynamic equilibrium



its value is 987°C, which agrees well with experimentally established magnitude contained within limits of 930-970°C.

For atmospheric pressure, when the entire chlorine is obtained in elementary form, the equation of combustion has the following form:



and the appropriate rated temperature is equal to 967°C.

The decrease in the quantity of oxide from 0.55 to 0.23 moles during the transition from atmospheric pressure to 70 at indicates that the nitric oxide is formed as a result of the oxidation of ammonia, and nitrogen - from the nitric oxide. In this case the decomposition of the nitric oxide at 1000°C proceeds too slowly in order that during the time of combustion it could form nitrogen in quantities established by the experiment. It is most probable that nitrogen is formed as a result of the interaction between the nitric oxide and ammonia. The decrease in the quantity of nitric oxide with an increase in pressure should be connected to the fact that the pressure more greatly affects the interaction of ammonia with the nitric oxide than the formation of it by means of the oxidation of ammonia.

The decrease in the quantity of nitrous oxide with an increase in transverse dimensions of the specimens or in the presence of a catalytic agent, possibly, is conditioned by the increase in the effective temperature of combustion, as a result of which a more reactive (in comparison with NO) nitrous oxide predominantly burns.

Adams, Newman and Robins [159] studied the dependence of the rate of combustion of ammonium perchlorate and mixing powders with it as a base upon a number of factors (dimension of the particles of the oxidizer and fuel, pressure, ratio of the oxidizer: fuel, and chemical composition of the fuel).

Specimens with a cross section of 0.5 × 0.5 cm and length of 8 cm were prepared by transverse pressing under a pressure of 500 kg/cm² and were burned in an atmosphere of nitrogen in unarmored form in

a bomb of constant pressure with windows. The rate of combustion was measured by the shadow method and was constant within the limits of $\pm 5\%$. The greatest variance was observed in the region of the independence of the combustion rate of pressure.

The rate of combustions of the ammonium perchlorate itself and to a lesser degree the lower limit of the ability to burn depend on the method of the preparation of perchlorate, and the main reason of this is, apparently, traces of admixtures. One of these admixtures - lead chloride, which in small quantities greatly retards the combustion rate. However, slow combustion was observed in the specimen containing lead. Hence, it follows that the admixture of lead, apparently, suppressed the action of some positive catalytic agent of combustion, which was contained in the rapidly burning perchlorate. In mixtures with fuel these distinctions are smoothed out.

The basic reason for the existence of the lower limit of the ability to burn under pressure is considered by the authors as being the decrease in the heat of combustion with a lowering of the pressure, which leads to the formation of a considerable quantity of nitric oxide.

The lower limit can be lowered by such changes owing to which the flame can be sustained at a lower temperature, for example, by the increase in the initial temperature, by the admixture of small quantities of fuel, or by the placing into the atmosphere of an ignitable gas. Thus, at atmospheric pressure combustion is propagated if the initial temperature is increased to 250°C ; in these conditions the measured temperature of combustion was 1200°K , which corresponds to the complete conversion to elementary nitrogen.

Dependence $u(p)$ can be expressed by the exponential law with the exponent of 0.5; near the lower limit the rate can drop with a decrement in pressure more rapidly; dimensions of the particles have only a slight effect on its magnitude.

Fuels can be divided into two basic groups: 1) those decomposing during heating with the formation of only gaseous products, for example, paraformaldehyde, hydrocarbons; 2) those which melt and are charred or only charred with the formation of the solid and gaseous phases, for example carbohydrates and acetylated hydrocarbons. These include carbon black. Since the dimension of the particles of the fuel has a negligible effect on the rate of combustion, dimensions of the particles of the fuel were taken as being constant.

Figure 133 gives the dependence $u(p)$ for the mixtures of ammonium perchlorate with polystyrene with a different content of the latter upon 0 up to an excess, which gives the same rated temperature of combustion as that of a pure perchlorate.

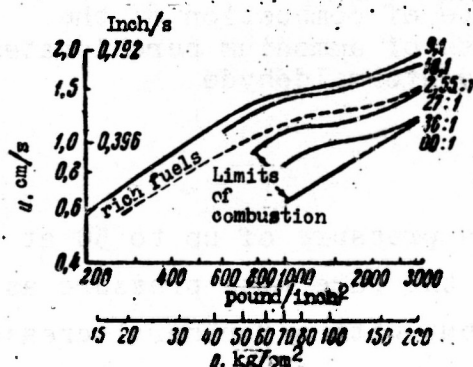


Fig. 133. Effect of the ratio by weight of the fuel to the oxidizer (numbers near the curves) on the rate of the combustion of the mixtures of ammonium perchlorate with a polystyrene. Dimension of particles NH_4ClO_4 is 74-105 μm and of polystyrene, <74 μm .

The exponent for a stoichiometric mixture below 60 at is between 0.5 and 0.6; between 60 and 100 at it decreases down to 0.25 and then increases again. From the graph it is evident also that with an increase in the polystyrene content, the rate of combustion rapidly increases, passes through a maximum at ~8% and then slowly drops. The mixture containing 28% polystyrene burns two times faster than does the perchlorate, although the rated temperature of their combustion are identical. The curve for the mixture with naphthalene is almost identical to the polystyrene curve. Experiments on the effect of the dimension of particles of the oxidizer indicated

that, starting from 100 μm and below, the decrease in the dimension of the particles to 60 μm does not affect the rate of combustion; at high pressures the mixture with small particles burns faster.

The rate of the combustion of mixtures with paraformaldehyde (Fig. 134) increases in proportion to $p^{0.5}$ up to 55 at; with a further increase in pressure the exponent is lowered and becomes equal to zero at 90 at. The greatest rate of combustion is observed with an excess of the oxidizer. With a decrease in the dimension of the particles (85-30 μm) the rate of the combustion of a mixture with 20% paraformaldehyde in an interval of 4-20 at increases.

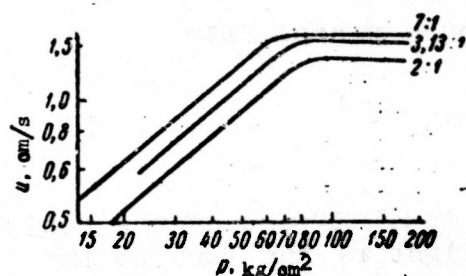


Fig. 134. Effect of the change in the ratio of the oxidizer to the fuel (numbers near the curves) on the rate of combustion of the mixtures of ammonium perchlorate with paraformaldehyde.

In mixtures with carbon black at a pressure of up to 50 at there is observed the same increase of the rate with pressure as that for the mixtures examined above, but with a further increase in pressure the exponent continuously increases, and above 100 at the rate could not be determined; the same increase in v is revealed for mixtures with saccharase which forms with thermal decomposition a solid carbonic residue.

The behavior of the stoichiometric paraformaldehyde mixtures, in which the part of the paraformaldehyde is replaced by carbon black (Fig. 135) is interesting. The presence of 1% carbon black removes the independence of the rate of combustion of pressure; 2.4% carbon black somewhat increases the rate at low pressures; above 70 at the dependence $u(p)$ slowly increases with pressure; at 7.3% carbon black curve $u(p)$ is almost identical to the curve of the mixture containing one carbon black.

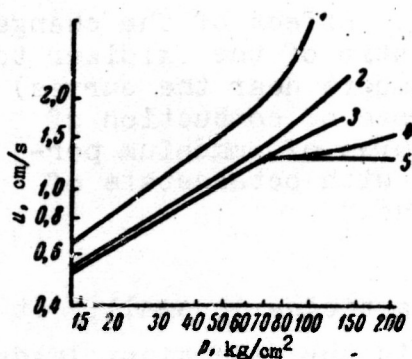


Fig. 135. Effect of carbon black on the rate of combustion of mixtures of ammonium perchlorate with paraformaldehyde. Perchlorate content - 75.6%, carbon black content: 1 - 7.3; 2 - 2.4; 3 - 1.2; 4 - 0.5 and 5 - 0%.

Curves of mixtures of different composition on the basis of cellulose acetate (Fig. 136) indicate a high rate with an excess in the oxidizer. Irrespective of the composition the interval of pressure where the rate does not depend on the pressure is observed. The effect of the dimension of particles of the oxidizer is different, than that in the case of mixtures with polystyrene. The decrease in the dimension of particles increases the rate of combustion; the section of the independence of the rate of combustion of pressure in curve $u(p)$ in this case is retained.

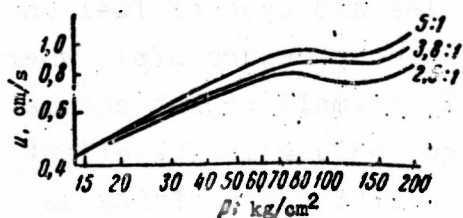


Fig. 136. Effect of the change in the ratio of the oxidizer to fuel (numbers near curves) on the rate of the combustion of the mixtures of ammonium perchlorate with cellulose acetate.

The effect of acetylated hydrocarbons on the dependence of the rate of combustion upon pressure was studied on mixtures on the basis of octaacetate of saccharase (Fig. 137). Up to 60 at the relationship of components weakly affected the rate of the combustion, although the maximum lay with the excess in fuel. At higher pressures the rate decreased with an increase in pressure and increase in fuel content. Above ~ 100 at it is less than the rate of combustion of pure perchlorate.

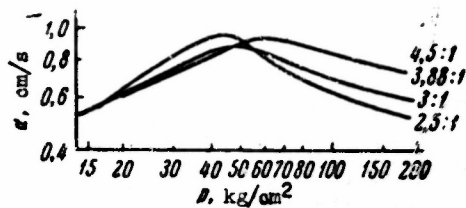


Fig. 137. Effect of the change in the ratio of the oxidizer to fuel (numbers near the curves) on the rate of combustion of the mixtures of ammonium perchlorate with octaacetate of saccharase.

The effect of the dimension of the particles is small: it appears in the direction that a decrease in the dimensions leads to an increase in the rate at low pressures and decreases it at high (Fig. 138).

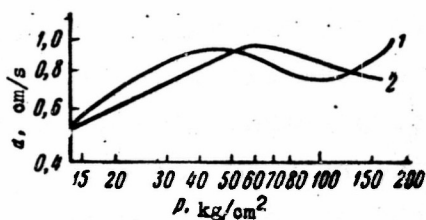


Fig. 138. Effect of the dimension of particles of the oxidizer on the rate of combustion of the stoichiometric mixtures of ammonium perchlorate with octaacetate of saccharase. 1 - dimension of particles, $< 50 \mu\text{m}$; 2 - $74-105 \mu\text{m}$.

The described results, obtained with end combustion, especially the effect of the dimension of the particles and type of fuel on the dependence of the rate of combustion upon pressure $u(p)$, where compared with experiments on combustion in a small rocket chamber ($d = 5 \text{ cm}$, $l = 15 \text{ cm}$, weight of the charge, $\sim 300 \text{ g}$). The effect of acetylated fuel was studied on the composition containing as binder cellulose acetate, dissolved in triacetin; the exponent was almost equal to zero in the whole studied interval of pressures from 35 to 150 at, and the rate in this case was changed from 0.5 to 0.533 cm/s. With end combustion the rate had a negative ν above 55 at, and the charge ceased to burn at 130 at.

Similarly studied was the effect of dimensions of the particles on the dependence of the rate of combustion upon pressure for the composition containing 89% perchlorate, 10% polyisobutylene and 1% wetting agent.

Experiments were conducted in two variants. In the first one the powder was prepared in two specimens of perchlorate - coarse-grained not subjected to atomization and pulverized to a specific surface equal to $2000 \text{ cm}^2/\text{cm}^3$. The level of energy of powder was changed by the replacement of part of the perchlorate by ammonium picrate. The results, given in Table 21, indicate that at pressures below 70 at, independently of the picrate content, the change in the dimension of the particles of the oxidizer has only a slight effect on both the rate of combustion and on its dependence on pressure. At higher pressures the coarse-grained oxidizer has a considerable effect especially in the case of compositions containing much fuel: at 20-50% picrate above 70 at the dependence of the rate of combustion upon pressure was absent. Below 20 and above 50% the dimension of the particles of the oxidizer also had an effect, but not so greatly.

Table 21. Effect of the dimension of particles of the oxidizer on the rate of combustion at different caloric value of the fuel.

Content in an intermixture of perchlorate and ammonium picrate, %		Combustion at 70 at, cm/s	Exponent at pressure of
NH_4ClO_4	ammonium picrate		
89 (M)	—	1,88	0,67
89 (K)	—	1,62	0,60
79 (M)	10	1,30	0,60
79 (K)	10	1,04	0,60 (to 70 at)
			0,375 (above 70 at)
69 (M)	20	0,94	0,54
69 (K)	20	0,87	Zero (above 77 at)
59 (M)	30	0,685	0,48
59 (K)	30	0,685	Zero (above 77 at)
49 (M)	40	0,485	0,46
49 (K)	40	0,485	Zero (above 70 at)
39 (M)	50	0,356	0,52
39 (K)	50	0,34	Zero (above 70 at)
29 (M)	60	0,27	0,52
29 (K)	60	0,25	0,66 to 70 at
			0,28 (above 70 at)

Note: M - finely divided; K - coarsely divided.

In the second variant of the experiment the picrate content was constant (30%). The oxidizer was extracted from the powder, and dimensions of its particles were determined. Various dimensions of particles of the oxidizer were obtained by the change in the portion of the coarse-grained perchlorate. Results of the experiments (Table 22) indicate the powerful effect of dimensions of particles on the dependence of the rate of combustion upon pressure. The greater they are, the less the rate increases, especially at increased pressures; with particles larger than those studied the rate even decreased with an increase in pressure. At pressures of 70 at and below, the increase in dimensions of the particles decrease the combustion, although at mixtures containing less than 10% (by weight) of fuel, this decrease is slight.

Table 22. Effect of the dimension of particles of the oxidizer on the dependence of the rate of combustion upon the caloric value of the fuel.

No. of group	Specific surface NH_4ClO_4 , cm^2/cm^3	Rate of combustion at 70 at, cm/s	Exponent at a pressure of
1	4500	0.685	0.48
2	3050	0.710	0.25
3	2500	0.66	Zero (above 77 at)
4	2620	0.710	Zero (above 70 at)
5	2300	0.66	Zero (70-98 at)
			-0.5 (above 98 at)
6	1920	0.635	-0.33 (above 77 at)

At higher pressures the dependence of the rate of combustion upon pressure is changed and becomes more sensitive to dimensions of the particles of the oxidizer and to the content and chemical nature of the fuel.

On the whole for volatile fuel the dependence of the rate of combustion upon pressure in the interval of 70-200 at decreases with an increase in dimensions of the particles, oxygen content in

the fuel and, possibly, fuel content. The exponent at p can be negative, and the rate of combustion is less than that of the ammonium perchlorate itself even for mixtures with the stoichiometric content of fuel.

In the case shown in Figs. 137 and 138, the sign of the effect of the change in dimensions of the particles of the oxidizer and the fuel: oxidizer ratio is changed, passing from the region of pressures with a positive value of v to the region of high pressures with a negative value of v .

The rate of combustion of the mixture of the ammonium perchlorate with polystyrene [160] can be more or less than that of the perchlorate itself, depending on the pressure, the composition of the mixture and the grain size (Fig. 139).

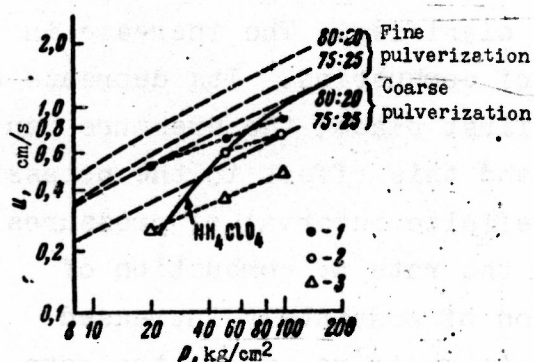


Fig. 139. Dependence of the rate of combustion upon pressure for a mixture of ammonium perchlorate with polystyrene (numbers near the curves - ratio of components) and other fuels. 1 - polystyrene resin 75:25; 2 - polysulfide resin 65:35; 3 - polyester 65:35.

For large grains of the oxidizer with its small content the rate of combustion of the mixture is higher at low pressures and less at high pressures than it is for pure perchlorate.

With a large content in the mixture of fine-grained perchlorate, the rate of combustion of the latter in the studied interval of pressures is higher than that of the pure oxidizer. Assuming that the rate of combustion of particles of perchlorate in the mixture in any case is not less than that of pure perchlorate, the authors conclude that mixtures burning more slowly than perchlorate itself, collars on a burning surface are more ignitable.

With this conclusion one should compare the data on the erosional combustion of some perchlorate mixtures, which indicate that at the increased pressures (100 at) and considerable rate of the gas flow (>100 m/s) the distinction in the magnitude of the rate of combustion disappears.

At average (50 at) and low (20 at) pressures the situation is different, and the effect of the increase in temperature continues to be apparent, although the effect of the composition of mixture (at 50 at) disappears. In this case, if at high pressures the rate of the nonerosional combustion is less than the rate of the combustion of the perchlorate itself, then the erosion removes the effect of the composition; if the rate of combustion is greater than the perchlorate, then the effect of the composition is retained with erosion.

The reasons for the decrease in the rate of the combustion of some quick-burning explosives and also the ammonium perchlorate with an increase in pressure are not clarified. The increase in pressure usually increases the rate of combustion. Its decrease can be interpreted in two ways: in the first place, the pressure can also retard the rate of combustion, and this effect in the potassium picrate and others prevail in the definite interval of pressures, and, secondly, some factors increase the rate of combustion of the indicated substances in the region of moderately increased pressures, and with further increase in pressure, where the rate falls, their effect does not appear, and the rate of combustion and also the increase with pressure have normal magnitude and behavior.

Some cases are known when the increase in pressure retards the rate of chemical reactions. This occurs, for example, on the upper limit of the chain reactions, when the break of the circuit is determined by triple collisions and its continuation by double collisions. If into the sequence of reactions there enters the reversible reaction of dissociation with subsequent monomolecular

conversion of one of its products, then the increase in pressure, by decreasing the concentration of the latter, can also retard the rate of the formation of final products. However, there are no specific foundations for assuming similar mechanisms in this case.

It is possible to imagine also physical reasons for the indicated correlation. If an exothermal reaction is developed through individual nuclei, then the presence in the contact with them of denser gas can soften the local heatings and decrease because of this the rate of the increase in the nuclei.

Further, during the combustion of solid substances dispersion of the substance can be very important; the increase in pressure, by decreasing the volume of the formed bubbles of gaseous products of dissociation, should impede dispersion.

In connection with the fact that the explosive for which there is revealed a maximum of the rate on curve $u(p)$ at high temperatures are liquefied as a result of fusion and decomposition, Svetlov and Fogel'zang propose that the decrease in the rate of combustion is conditioned, namely, by this liquefaction which approaches with combustion under increased pressures and retards the rate of chemical conversion. It is possible to imagine the indirect effect of liquefaction. If dispersion during combustion is carried out as a result of the boiling of the liquid intermediate product, then the increase in pressure, by increasing its boiling point, will decrease the dispersion and, consequently, the rate of combustion.

Finally, it is possible that in this case the effect of the pressure is connected with a factor substantially new for the theory of the combustion of explosives. It is known that under definite conditions the combustion of many explosives, specifically, quick-burning, occurs unevenly and pulsating. Between the oscillations of pressure and other parameters of combustion and the charge or its parts with definite relationships between the periods of oscillations there can occur resonance, which leads to the reciprocal

intensification of the oscillations. The intensification of oscillations in the zone of combustion can, by intensifying dispersion, accelerate the combustion. It is possible also that it can transfer the combustion of each of the particles, which are formed as a result of dispersion, from a diffusion-conductive into convective mode; correspondingly, the time of combustion of particles decreases and the zone of maximum temperature approaches to the burning surface - the rate of combustion increases. In the range of conditions of combustion where resonance is absent, the rate of combustion has the usual low value; after the drop the rate of combustion of the potassium picrate is close to the rate of combustion of picric acid and thus slowly increases with pressure.

Shidlovskiy [161] studied the combustion of ammonium salts of nitric perchloric, iodic and chromic acids in a manometric bomb. Pressed pellets were ignited by black powder in charges which created a pressure of 75 at (in experiments with nitrate) to 120 at (in experiments with remaining salts). The first three salts burned completely and the chromate - partially. The duration of combustion in parallel experiments for a nitrate greatly fluctuated (0.57 and 0.93 s); corresponding there was a difference (because of heat losses) in maximum pressure (580 and 410 at). Perchlorate burned more rapidly and more uniform with respect to pressure and time. Iodate occupied an intermediate position.

Under conditions of the bomb of constant pressure, with experiments of Glazkova [162], ammonium nitrate, poured into a small glass vessel, does not burn even with a diameter of 35 mm and pressure of 1000 at. Waterproof saltpeter, which contains small quantities of iron salts of fatty acid, can burn in Plexiglass tubes with a diameter of 7 mm starting from 210 at. The rate of combustion very weakly increases with the pressure, and at 1000 at it is a total of $1.5 \text{ g/cm}^2\text{s}$. With the other catalytic additions (K_2CrO_4 , PbCrO_4 , $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$) and in large quantities (5%) the rate is more and at 1000 at atmosphere is included between 1.8 and $2.7 \text{ g/cm}^2\text{s}$. The effect of chloride (NaCl , BaCl_2 and CrCl_3) was also studied. Saltpeter with 7% NaCl starts to burn at 12 at. The

rate increases linearly also relatively rapidly up to 200 at and slowly from 200 to 1000 at. Saltpeter with 10% barium chloride starts to burn from 27 at; according to its effect on the rate of combustion of saltpeter this chloride is close to common salt, somewhat distinguishing from it by the nature of curve $u(p)$.

Trotyl relatively slightly increases the ability of ammonium saltpeter to burn. For the mixture of saltpeter with trotyl (80:20) in tubes with a diameter of 7 mm the critical pressure of combustion is 145 at. Another distinction of the mixture is the small rate of combustion and its weak increase with pressure (Fig. 140); at 1000 at the rate of combustion is a total of 5 g/cm²s, and for trotyl, which is close with respect to the heat of a combustion, - 6.5 g/cm²s.

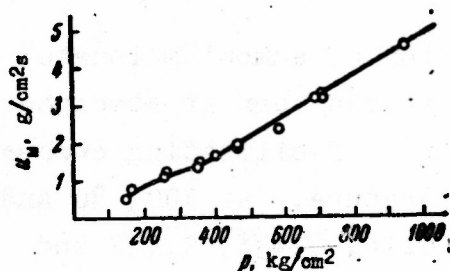


Fig. 140. Dependence of the rate of combustion of ammatol 80:20 upon pressure.

In the interval of pressures of 150-350 at the rate of combustion increases with the increase in pressure not linearly, but somewhat more slowly, starting from 400 at, the dependence of the rate upon pressure can be expressed by the ratio

$$u_M = -0.58 + 0.00554 p.$$

Unlike the trotyl mixture, the mixture of ammonium nitrate with charcoal (91.4:8.6) can burn in tubes with a diameter of 7 mm even at atmospheric pressure, although the rate of its combustion at high pressures is low and slowly increases with pressure. In the interval of 25-1000 at it can be expressed by the ratio

$$u_M = 0.0156 p^{0.778}.$$

The introduction into the composition of a trotyl mixture of 5% potassium bichromate greatly increases both the ability to burn and its rate (Fig. 141); the potassium chromate on the combustion similarly affects the carbon mixture (Fig. 142). A considerable effect of catalyzers indicates the fact that the low rate in their absence is determined by the slowness of the occurring exothermal reactions.

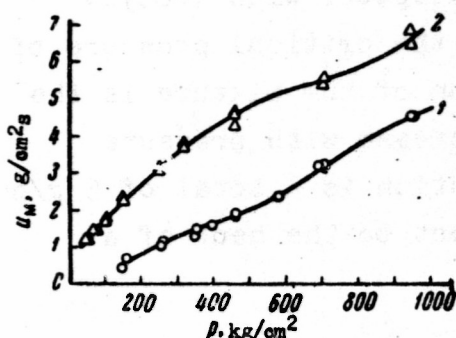


Fig. 141. Effect of potassium bichromate (5%) on the rate of combustion of amatol 80:20. 1 - amatol 80:20; 2 - amatol 80:20 + $K_2Cr_2O_7$.

Catalytic agents affect the combustion of ammonium iodate; in the presence of potassium bichromate it can burn at atmospheric pressure (diameter of the charge, 17.5 mm). Facilitating combustion also is the increase in the initial temperature. At 100, 80 and 60°C the rate of combustion is, respectively, 0.138, 0.132 and 0.090 g/cm²s.

Hydroxylaminesulfate $(NH_3OH)_2SO_4$; effective catalytic agents for this compound are cuprous chloride, especially anhydrous, and the manganese dioxide. At 100°C and atmospheric pressure the hydroxylaminesulfate is also able to burn (diameter of the charge, 20 mm), and the rate of combustion is 0.07 cm/s.

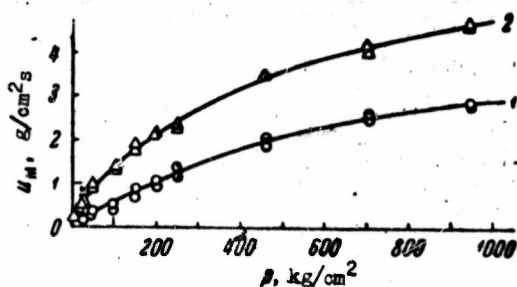


Fig. 142. Effect of potassium chromate on the rate of combustion of ammonium nitrate with charcoal. 1 - dynammon 91.4:8.6; 2 - mixture containing 82% NH_4NO_3 , 8% carbon and 10% K_2CrO_4 .

Experiments on the pressed ammonium dichromate indicated that in charges with a diameter of 20 mm it is able to burn, starting from 1 at, and the rate of combustion in the interval of the pressures of 1-20 at increases almost in proportion to the pressure.

With the combustion of unarmored cylindrical charge in a manometric bomb the average rate of combustion was $4 \text{ g/cm}^2\text{s}$ at an average pressure of $\frac{80+640}{2} = 360 \text{ at}$. The rate of combustion at atmospheric pressure was determined also at different temperatures from room to 150°C (at -70° the dichromate under given conditions of the experiment did not burn). It increases greatly with temperature, comprising at 18° - 0.035 , at 95° - 0.11 and at 150° - $0.16 \text{ g/cm}^2\text{s}$. The rate of combustion of ammonium trichromate $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$; at 0.5 at it was 0.038 and at 5 at - 0.5 cm/s . The increase in temperature from 20° to 98° increased the rate of combustion of trichromate at atmospheric pressure by two times.

6. Combustion of Explosives at Ultrahigh Pressures

All the examined data on the dependence $u(p)$ are referred to pressures exceeding 1000 at. At somewhat higher pressures (up to 4000 at) the rate of combustion of some explosives was determined by Belyayev and collaborators [120]. Experiments were produced in a manometric bomb with armored cylindrical charges consisting of sequentially located layers of pressed (under a pressure of 4000-5000 at) explosives with a different rate of combustion, the combustion of which in curve $p(t)$ was depicted by steps with a different slope (see Fig. 84). Furthermore, the method of ionization sensors was used. The results of the experiments are shown on Fig. 143. The rate of the combustion of trotyl and PETN increases with pressure linearly and is almost proportional to it. Also dependent on pressure is the rate of combustion of the mixture of ammonium nitrate with trotyl. At 3000 at the dot for PETN lies somewhat above the straight line, which is a supposedly connected with the disturbance of laminar combustion. For mixtures of the

potassium perchlorate with bitumen and with trotyl, the rate of combustion increases not in proportion to the pressure but more slowly. This deviation in the rate from the proportionality to pressure is especially noticeable in black powder. Up to 2000 at the rate of its combustion increases slowly; at 2000 at the maximum value of the rate of ~ 6 cm/s is attained, which with a further increase in pressure no longer increases. The authors assume that the slighter (than the direct proportionality) dependence $u(p)$ for mixtures is more their common feature, and for various mixtures it appears in different intervals of pressure - for the mixture of bitumen with the potassium perchlorate earlier, for the trotyl mixture later, and for the mixture of trotyl with ammonium nitrate this development should be expected at even higher pressures lying above the interval of pressure studied in this work.

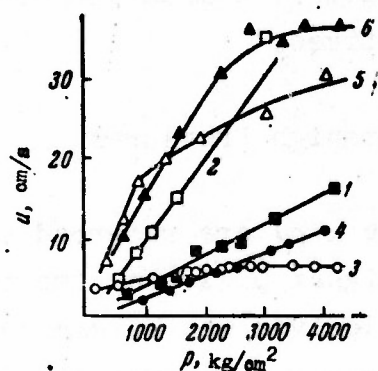


Fig. 143. Dependence of the rate of combustion upon pressure. 1 - trotyl; 2 - PETN; 3 - smoky powder (DRP-3); 4 - mixture of 79% ammonium nitrate and 21% trotyl; 5 - mixture of 86.6% KClO_4 and 13.4% bitumen; 6 - mixture of 61.5% KClO_4 and 38.5% trotyl.

The reason for the retarding of the increase in the rate in the region of the high pressures is the predominant importance, which under these conditions the diffusion obtains, which limits the rate of the reaction in the front of combustion.

Very interesting data on the combustion of a number of explosives, including those igniting at the ultrahigh pressures up to 12,000 at, were obtained by Muraour and Basset [163]. Experiments on lead azide were conducted in the following manner. An explosive in the

form of small clamps or pellets, pressed under a pressure of 3000 at, were placed on the lining of a small sheet of mica or brass plate in a chamber of high pressure with a capacity of 25 cm³. By admitting an appropriate gas, the necessary pressure was created, whereupon the explosive was ignited by a platinum wire being heated by current.

At atmospheric pressure the detonation of azide makes a hole in the brass with a diameter of 10 mm; in a medium of nitrogen, condensed to 1000 kg/cm², the diameter of the opening decreases to 4 mm. The mechanical action of the explosion at a pressure of 3000 at becomes even less, and starting from a pressure of 5000 at, it is practically absent. With the replacement of nitrogen by argon, condensed to 9000 at, the lead azide by nitrodiazobenzene perchlorate, and also in the replacement of rapid heating of the wire by slow heating at a pressure of 10,000 at, the results of the experiment did not change. Thus, at ultrahigh pressures the lead azide and nitrodiazobenzene perchlorate burn, not producing a mechanical action. A possible reason of this effect is the dilution of explosives by gas of considerable density filling the space between particles and also gas being dissolved in the explosive. Besides this, at ultrahigh pressures the distinction in density between the initial explosive and gas products of combustion is greatly reduced. This decreases the dispersive action of the latter, which is the basic factor which determines the high rate of combustion and its change into detonation.

Similar experiments at ultrahigh pressures with fulminating gelatin and pressed picric acid showed that in these conditions they also burn without giving detonations.

7. Smokeless Powder

The combustion of smokeless powder was studied in various intervals of the pressures. During a long period of time, when the sole region of the application of powder was in firing barrel

weapons, there was practical interest in pressures of several hundreds to 3000 at. Investigations in this range of pressures were produced basically with the help of a monometric bomb and led, especially in the numerous works of Muraour and his colleagues, to the confirmation of the linear dependence of the rate of combustion upon pressure $u = A + Bp$. In this case the term A is small, and therefore at the high pressures the linear dependence can be replaced by the expression of direct proportionability which because of its simplicity was widely used in the interior ballistics of barrel weapons.

Subsequently, in connection with intense interest in the relatively low pressures at which powder burns in jet engines, and also for the clarification of the mechanism of combustion, they began to examine the region of low pressures - from atmospheric to several hundreds of atmospheres, and also the combustion in a vacuum - from fractions of a millimeter up to an atmosphere. In two works the combustion of powders at the ultrahigh pressures - up to 10,000 and even 60,000 at was studied also.

In accordance with the increase in the interval of pressure appropriate investigations will be examined.

Pokhil [164] studied the combustion of pyroxylin powder with its heating in a vacuum up to spontaneous ignition and with artificial ignition.

The combustion which appears as a result of spontaneous ignition occurs differently according to its external criteria depending on pressure. At a pressure (finite) below 2 mm combustion occurs flamelessly and with a relatively high rate. Above 2 mm cold-flame combustion, which is accompanied by light emission of a dark blue color is observed. With an increase in pressure above 2 mm the height of the cold-flame zone increases, and starting from ~10 mm at a distance of 7 mm over the surface of the powder there appears a second bluish yellow flame, which, unlike the cold flame, is apparent during the combustion of the powder in daylight. If the

powder is ignited at pressures above 10 at, then at a considerable distance over its surface there appears a tongue of a flame of yellow color, which is intensified with pressure with respect to illumination and approaches to the surface of the powder. The pressure at which this flame appears is decreased with an increase in initial temperature of the powder and with an increase in the diameter of the charge.

The combustion of powder in a vacuum is accompanied by the formation together with the gases of a large quantity of smoke - up to 70% during flameless combustion. With the increase in pressure the quantity of smoke decreases - up to 50% at 20 mm and up to 30% at 100 mm; however, it is observed at considerably high pressures: even at 100 at about 0.6% smoke is formed. The quantity of smoke also depends upon the initial temperature, decreasing with its increase. With respect to color, the smoke, which is formed at low pressures, is not distinguished from finely ground powder, and with ignition it burns with a yellow flame. With an increase in pressure the smoke becomes more finely dispersed and darker.

With the help of thin thermoelectric couples the temperature on the surface of the burning powder and its change with distance were measured. From Fig. 144 it is evident that with flameless combustion this temperature is 280-300°C, and the maximum of temperature ($\sim 330^\circ$) is reached at a distance of ~ 2 mm. At a pressure of 3-4 mm the maximum of temperature is higher ($\sim 400^\circ\text{C}$). At 5-7 mm - with the appearance of the second flame - the maximum of the temperature is considerably more (600-700°C) and is located much further from the surface of the powder.

The same types of flames are observed with artificial ignition of the powder, heated to a temperature less than that at which spontaneous ignition occurs. In this case the interval of pressure at which there is observed a flameless or, respectively, cold-flame combustion is wider; the greater this interval, the lower the temperature. Thus, at 90°C the powder burned flamelessly up to a pressure of 20-30 mm instead of 2 mm with spontaneous ignition.

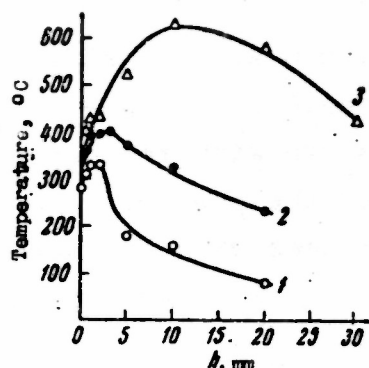


Fig. 144. Dependence of temperature on distance during the combustion of pyroxylin powder. 1 - flameless combustion ($p_{\text{KOH}} \leq 2$ mm); 2 - cold-flame combustion ($p = 3-4$ mm); 3 - two-flame combustion ($p_{\text{KOH}} = 10$ mm).

In comparing the temperature on the surface of the powder during flameless combustion ($280-300^\circ$) with the initial temperature ($85-90^\circ\text{C}$), Pokhil, by assuming that combustion occurs without heat losses into environment, concluded that the thermal effect of the reaction in condensed phase is $q = 0.4 (280-85) = 80$ cal/g, where 0.4 is the heat capacity of the smoke-gas mixture being formed.

The dependence of the rate of combustion upon pressure is unique (Fig. 145). In the region of flameless combustion, i.e., low pressures, the rate remains of constant; at high pressures it increases linearly $u = A + 0.23 \cdot (p - 0.026)$; for nitroglycerine powder $u = 0.05 + 0.315 (p - 0.04)$.

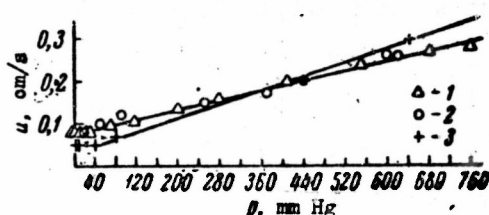


Fig. 145. Dependence of the rate of combustion of pyroxylin powder upon pressure. 1 - in an atmosphere of nitrogen; 2 - in atmosphere of products of combustion; 3 - for nitroglycerine powder (in an atmosphere of nitrogen).

The temperature near the surface was measured and at higher pressures when the powder in the columns of the diameter used burns at room temperature. From Fig. 146 it is evident that the increase in pressure leads to an increase in the maximum of temperature and approaches it to the surface of the powder. An increase in diameter of the specimen increases the temperature of combustion. An increase in pressure leads to an increase, although comparatively weakly, also of the temperature of the surface layer of the burning powder (Table 23).

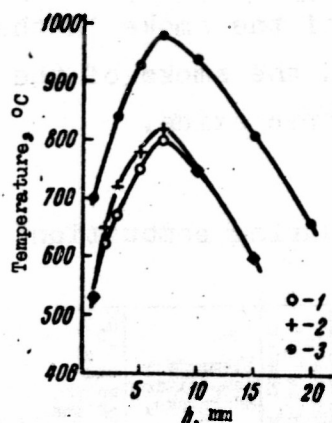


Fig. 146. Dependence of temperature on distance in the zone of a smoke-gas mixture. 1 - pyroxylin powder ($d = 5$ mm); 2 - nitroglycerine powder ($d = 5$ mm); 3 - nitroglycerine powder ($d = 10$ mm).

Table 23. Approximate values of temperatures in the zone (in °C) over the surface of the powder depending on distance at $p \sim 5$ [atm(abs.)] (diameter of the powder specimen, 4-5 mm).

Zone over the surface of the powder (h), mm	Pyroxylin powder	Nitro-glycerine powder	Zone over the surface of the powder (h), mm	Pyroxylin powder	Nitro-glycerine powder
1	530	530	7	800	820
2	620	650	10	750	750
3	670	720	15	600	600
5	750	780	20	400	400

The composition of the gas and condensed products of combustion at different pressures (Table 24) was determined. With flameless combustion an especially great many nitrogen oxides and half of them - nitrogen dioxide are formed. The content of the ignitable gases and products of oxidation is disproportionately small. Apparently, in the first stage of combustion there occurs predominately the cleaving of oxygen, connected with nitrogen, and oxidizing reactions occur in a much smaller amount.

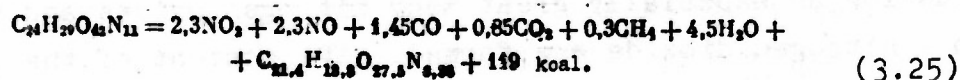
With an increase in pressure the formation of NO_2 rapidly drops, and the content of NO in the beginning increases and then slightly decreases; quantities of CO and H_2O considerably increase. Comparing these data with the decrease in the quantity of smoke and the enrichment of it by carbon, one should conclude that the change

in composition of the gas phase occurs predominantly because of the gasification of the nitrogen and oxygen of the smoke in the form of nitric oxide and the interaction with the smoke of the nitrogen dioxide with its transition into nitric oxide.

Table 24. Composition of products during combustion under different conditions.

Pressure, mm Hg	Percent of the volume of the gas phase								Smoke, % of weight of powder	Elementary composition of "smoke," %	H ₂ O, % of the weight of the powder
	NO ₂	NO	CO ₂	CO	CH ₄	H ₂	unsatu- rated hydro- carbons	N ₂			
< 2 (flameless combustion)	32	32	12	20	4	—	—	—	70	C 32,2 O 54,7 H 2,1 N 11,0	7,2
~ 12 (two-flame combustion)	15	44	13	25	3	—	0,3	1,6	42-50	C 50-55 O 38-42 H 2-1,5 N 6-4	13,6
~ 100 (two-flame combustion)	4	38	14	37	4	—	0,3	2-3	20-30	C 65-70 O 30-34 H 2-1 N 1	15,0

On the basis of the given tables the equation of flameless combustion of the powder has the following form:



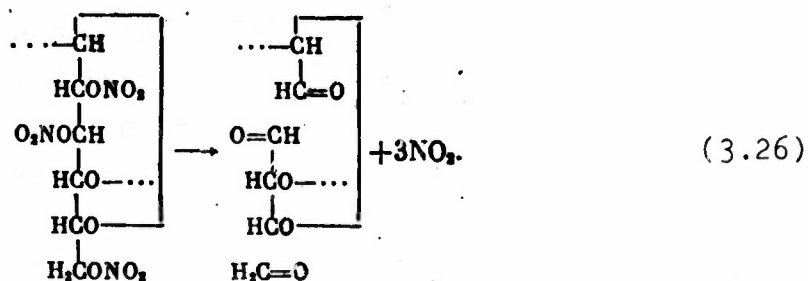
Pohkil assumes that at relatively high pressures the combustion of the powder goes through the stage of the formation of the fume. In order to detect it, the charge powder was inserted tightly into a metal cylinder; introduced into it up to the surface of the powder was the perforated plunger, through the openings of which gaseous products with smoke emerged during a combustion. Under these conditions of the experiment the quantity of smoke was much more (for example, at 100 at, 10 times), than under the

usual conditions of combustion. Inasmuch as the quantity of the trapped smoke depends on the intensity of the process of stagnation, and also inasmuch as the temperature of the surface only very slightly depends on the pressure, Pokhil considers it experimentally proven that the mechanism of the combustion of powders of the colloidal type in the range of increased pressures is the same as that in a vacuum, i.e., in both cases a large quantity of smoke initially is formed.

The formation of a powdery residue ("white substance") during the combustion of nitrocellulose at low (below 5 mm Hg) pressures was also observed American investigators [165]. The greater part of this residue consists of partially denitrated and oxidized nitrocellulose with an average molecular weight of about 1500. Low-molecular products - formic and oxalic acids, furfurole, glyoxal and formaldehyde, nitric oxide and carbon monoxide, hydrogen and water are formed also.

At high pressures the decomposition becomes more complete. At 100 mm about 40% of the charge was obtained in the form of a complex of liquid products ("red substance"), which consists of mainly glyoxal, formic acid, formaldehyde, water and small quantities of glicerine aldehyde; mesoxalic aldehyde and other more complex compounds.

For the initial reactions leading to the formation of a "red substance," authors propose the following diagram:



The first stage is the breaking of bonds RO-NO_2 with subsequent regrouping of free radicals being formed and the breaking of the carbon-carbon bonds 2-3 and 5-6. According to this diagram glyoxal is obtained from carbon atoms 1 and 2 by the hydrolysis of acetal bonds. Formaldehyde is formed from the carbon atom 6; carbon atoms 3, 4 and 5 form aldehydes with a trinomial chain detectable in the products of combustion. Further reactions between NO_2 and these initial products leads to more deeply oxidized compounds, detectable in the "red substance." The further increase in pressure decreases the quantity of the formed "red substance," but aldehydes are contained in the products of combustion up to pressures of several atmospheres.

Experiments on nitroglycerine and dinitrodyethyleneglycol powder [164] indicated the same three types of combustion at reduced pressures; somewhat higher was the necessary temperature of preliminary preheating ($110-115^\circ$) and the temperature on the surface ($300-310^\circ\text{C}$); the formation on the burning surface of a liquefied boiling reaction layer was observed more clearly.

Heath and Hirst [166] studied at moderately increased pressures (up to 140 at) combustion on the end of the armored small cylinders of cordite [nitrocellulose (12.2% N) - 48%, nitroglycerine - 41%, carbamate - 9%, potassium cryolite - 2%] in a bomb of constant pressure in a flow of nitrogen. Besides the measurement of the rate of combustion, the thickness of the dark zone and zone of the flame at different pressures, there were produced spectrographic measurements of the zone of the flames, which indicated that the spectra of its radiation is continuous, and the color and brightness temperature are identical ($<2340^\circ-2370^\circ\text{K}$), i.e., the radiation has the nature of the radiation of an ideal black body. The probable emitters are particles of carbon, which are formed in the course of combustion. The measured temperature is lower than the rated (2470°K at 70 at) by $80-100^\circ\text{C}$ because of losses of heat by radiation. Below 7 at cordite ($d = 6 \text{ mm}$) does not burn, and a

bright flame appeared above 18 at. The rate of combustion grew with pressure according to expression $u = Bp^v$, where $v = 0.56$. The dependence of the thickness of the dark zone upon pressure can be expressed by the ratio $S = C/p^\alpha$, where $\alpha = 1.9$, unlike data ($\alpha = 3$) of Crawford, obtained for the powder of another composition.

Photographs of the burning surface show the presence on it of bright small bubbles and black balls smaller in dimensions and the general form of the surface is similar to the surface of a liquid, on which the burning balls regularly appeared and disappear so that the total number remains constant. The lifetime of the ball (milliseconds) decreases with an increase in pressure, and their concentration (per unit surface), on the contrary, increases; the dimension of the ball is 0.01-0.03 mm. Apparently, these balls are the small bubbles formed on the liquefied surface of the powder, in which there are reactions finished by the formation of the flame, which, when the bubbles burst, rises to the basic flame zone. Black balls are much more long-lived and supposedly are not small bubbles, but are formed in inorganic components of powder.

Apparently, only the very thin layer of powder adjacent to the surface of the grain takes part in the combustion. With a decrease in the rate of combustion the thickness of the heated layer rapidly increases, and the thermal effect of exothermal reactions occurring in it comprise a larger and larger portion of the total energy necessary for the sustaining of combustion. The quantity of heat liberated because of the reaction in the condensed phase can increase with a decrease in pressure and rate of combustion. It is experimentally established that for the majority of the powders on solvent volatilizing with difficulty, the dependence $u(p)$ becomes less at reduced pressures. In exactly the same manner the slowly burning powders reveal the smaller dependence $u(p)$ in the region of low pressures than quick-burning powders do.

Inasmuch as rocket engines for the greater part operate at the comparatively low pressures - below 140 at, then reactions in the condensed phase can have great practical importance and deserve thorough study.

By estimating the temperature of the surface of the burning powder by the method of the melting and decomposition of small particles of the alkali earth carbonates introduced into the powder, Daniels, Wilfong and Penner [167] assume that it exceeds 1000°C. This estimation, apparently, is overstated, inasmuch as the surface of the powder does not glow, and is conditioned by catalytic reactions on the surface of solid particle, as this has been established in attempts of measuring the temperature of a flame by bare thermoelectric couples. Another possible source of error is that solid particles can protrude over the surface of the powder and thus fall into the region of flame with high temperature.

Leypunskiy and Aristova [168] measured calorimetrically the heat reserve of the rapidly extinguished grain of powder and, on the basis of Michelson's temperature distribution, calculated the temperature of the surface of the powder. For nitroglycerine powder it was $330 \pm 45^\circ$ and for pyroxylin, $252 \pm 48^\circ$. Inasmuch as the experiments were conducted at atmospheric pressure, when the role of the reaction in the condensed phase was considerable, and calculation was produced without allowing for this fact, the error in determining T_s can be considerable.

The temperature of the surface can be determined also by direct measurement of the temperature profile with the help of thermoelectric couples. In this case the linear dependence of $\lg (T - T_0)$ upon x should be observed. In the region of low temperatures this relationship is fulfilled, and at increased temperatures a considerable curvature, obviously, conditioned by the heat release in the condensed phase, is observed. If the plane where there begins deviation is accepted as the surface of combustion, then its temperature is obtained for pyroxylin powder at $\sim 250^\circ$, which can be somewhat understated, inasmuch as the thermal effect of the reaction is not taken into account.

Although it is impossible to consider both of the examined methods reliable, one should assume that the temperature on the surface of the burning nitroglycerine powder is 300°C.

For typical nitroglycerine powder the thickness of the dark zone in its dependence on pressure is expressed by the relation

$$l = \frac{10^7}{P^2}.$$

The thermal effect of reactions which finished in the dark zone constitutes about 500 cal/g, i.e., less than half of the complete thermal effect. Correspondingly, the composition of products of reaction is changed (Fig. 147). In the region of the dark zone there is formed a considerable quantity of nitric oxide, which is reduced in the zone of the flame. In this zone the quantity of carbon monoxide decreases, and the quantity of CO₂ increases in the same way as the quantity of hydrogen which is formed according to the reaction of the water gas.

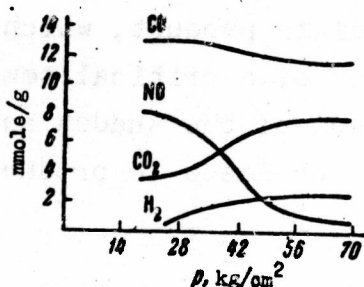


Fig. 147. Change in products of combustion of fuel HES4016 with an increase in pressure of the inert gas.

Thus, the flame of the combustion can be divided into two regions - dark and glowing with substantially different features in which various chemical processes occur. The part of the dark region adjacent to the surface of the powder is called by American investigators the zone of hissing, inasmuch as gas products will flow out at right angles to the surface of combustion with a considerable rate, which causes a hissing sound. The nature of the outflow of products of combustion indicates the fact that the reaction basically occurs very close to the burning surface. As

one would expect, the temperature gradient near the burning surface increases with pressure, inasmuch as it accelerates the gas-phase reactions. The temperature profile of the zone of combustion was measured [169] with the help of thermoelectric couples (Fig. 148). This zone is very narrow (several hundredths of a centimeter), considerably less than the dark zone at the same pressure. Beyond this narrow reaction zone the temperature rises to the level of 1400°C , at which it remains to the end of the dark zone. This temperature is confirmed by results of the spectroscopic measurement of the intensity of absorption bands NO. This method, although it is less accurate than the method of thermoelectric couples, has that advantage that no extraneous body is introduced into the flame. The calculations, founded upon the measurement of the heat of reactions of the dark zone and on the analysis of products being formed in it, lead to similar values of its temperature. The nature of the change in a temperature in the dark region indicates that its external regions are comparatively little active. The reason for this delay in the advance of the final series of reactions is unknown. It can be compared with the induction period, which is frequently observed in the presence of gas reactions. The exhaustion of the substance, which breaks the chains, the formation of the critical concentration of the intermediate product, which is automatically catalyzed, or the achievement of a critical temperature for a thermal explosion can be the reason of the sudden and the sharp intensification of the reaction, which leads to products which correspond to chemical equilibrium.

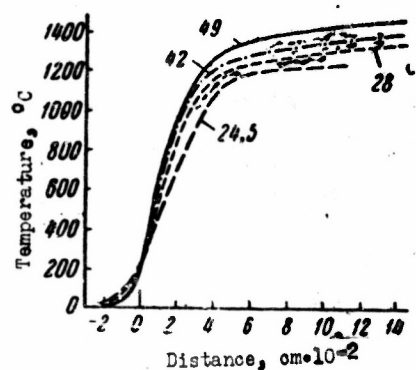


Fig. 148. Experimental profiles of temperature during the combustion of powder containing nitrocellulose with 13.5% nitrogen + 1% ethylcentralite. It is proposed that the temperature on the surface is equal to 250°C ; numbers near the curves - pressure (in kg/cm^2).

The normal rate of the combustion of powder and the nature of its dependence on properties of the powder and conditions of combustion have an extremely great importance for the determination of the usefulness of the powder as a reactive fuel. The detection of factors which affect the rate of combustion is a basic assignment and goal of the study of the mechanism of the process of combustion. In turn the study of the effect of any factor on the rate of combustion can give substantial information about the mechanism of combustion. It is expedient to use both ways: in the first place, examine the dependence of the rate of combustion upon characteristics of the powder and external conditions and, where it is possible, connect this dependence causally to the mechanism of combustion; in the second place, use data of the empirical study on the rate of combustion for the development of the qualitative picture of the process of combustion.

The dependence of the rate of combustion upon pressure is frequently expressed by the equation of more general form:

$$u = A + Bp^n. \quad (3.27)$$

However, for the greater part of mixing powders, for many ballistite powders containing various catalytic agents of combustion, and for the majority of powders at very low pressures, even this expression is not sufficient for a description of the real dependence of the rate of combustion upon pressure. Apparently, this dependence cannot be expressed by some simple law.

The available experimental data allow making the following generalizations.

1. At relatively high pressures (higher than the limit, lying between several tens of atmospheres and 140 at) depending on the composition, the law of combustion is a monotonic function of pressure and can be expressed by equations $u = Bp^n$, $u = A + Bp$, or what is more, $u = A + Bp^n$.

2. At intermediate pressures the dependence of the rate of combustion upon pressure can be more complex and greatly conditioned by the composition of the powder. (Sometimes intervals of pressures are observed in which the rate does not depend upon pressure or even decrease with its increase).

3. At very low pressures the extrapolation of the rate of pressure equal to zero gives its final value, although the powder stops burning at the pressures lying somewhere between the fractions of the atmosphere and tens of atmospheres.

From the point of view of the mechanism of combustion, apparently, at high pressures the greater part of the energy necessary for causing the surface decomposition (which conditions movement of the surface, i.e., the rate of combustion) enters from the high-temperature flame. The rate of the transfer of energy is determined by the thermal conductivity of the flame and by its distance from the burning surface. Inasmuch as the rates of reactions in the flame greatly depend on pressure, the increase in the latter leads to an increase in the transfer of energy and, consequently, to a smooth increase in the rate of combustion.

At intermediate pressure the zone of the flame is removed from the burning surface or is entirely absent. The considerable part of energy necessary for the sustaining combustion enters from the zone of hissing. Reactions in this band are inert, but they can be accelerated by catalytic agents. They greatly depend on the composition of the powder in contrast to the flame reactions, which are practically identical for all ballistic powders. As a result the dependence $u(p)$ is more greatly discriminated in this region.

At very low pressures very little energy returns to the burning surface from the gas phase, and the rate becomes almost independent of pressure. The source of energy independent of pressure becomes at the very low pressures (atmosphere or below) the reaction in the condensed phase.

*Dependence of the rate of combustion
upon the initial temperature*

The change in the rate of combustion of powder with the change in its initial temperature is comparatively little - usually less than 0.5% per degree and frequently even less. An attempt to connect this low temperature coefficient to the energy of activation of the leading reaction leads either to improbably small values of the energy of activation or to too high values of the temperature of the surface. However, apparently, such a simple analysis of the temperature dependence is impracticable in this case. The reaction does not occur isothermally but in the region of a very high temperature gradient where the accurate application of the concept of the energy of activation becomes difficult. The determining rate of combustion is the rate of the admission of energy to the powder; the temperature in the reaction zone is adjusted in order to sustain an appropriate rate.

The increase in initial temperature of the powder causes an increase close in magnitude in the final temperature of the flame, the accurate value of which can be calculated by allowing for the heat capacity of the powder and products of the reaction.

It is possible to assume that the temperature profile rises approximately by an identical magnitude at all points. However, the temperature of the burning surface cannot rise itself by this magnitude, inasmuch as due to the increase in the rate of combustion the surface layers during a short time obtain energy from the flame and reactions in the condensed phase. Therefore, the temperature on the burning surface will rise but by a smaller amount than do T_0 and T_{HOH} will be required.

The effect of the initial temperature on the rate of combustion can be examined: a) by taking into account the increase in temperature and, respectively, heat transfer from the flame to the powder and b) taking into account that less energy for the heating of the powder up to temperature T_n will be required.

Corner [170] calculated that with an increase in the initial temperature by 10°C the rate of combustion of cordite SC must grow by 2.2%; an experiment gives the values lying between 3 and 4%.

The equation

$$u = \frac{cP^n}{T - T_0}, \quad (3.28)$$

expresses the dependence of the rate of combustion upon the initial temperature. T' is the constant dependent on the composition of the powder and having dimensionality of the temperature; it corresponds to the temperature at which the rate becomes infinite, i.e., at which combustion would occur in the whole grain. Values of T' , obtained by extrapolation, consists of between 200° and 350°C, which is in reasonable agreement with the estimate of the temperature of the surface and temperature of the flash.

In accordance with these considerations the powder with a high value of T' should have a low temperature coefficient. Experimentally it was established that powders which contain relatively stable components, for example, dinitrotoluene, and which respectively have a higher temperature of decomposition than that of "hot" compositions, usually indicate the lesser dependence of the rate of combustion upon temperature. Many mixing powders, in which as a result of the exceptionally high stability of their components one should expect a high temperature of the surface, are also known by their low temperature coefficients.

At the high pressures the rate of combustion is supposedly determined by the final temperature of combustion, and the effect of the reactions in the condensed phase can be neglected. At low pressures the role of reactions in the condensed phase cannot be disregarded. Therefore, it is no wonder that the temperature dependence at low and intermediate pressures is more complex.

There are powders with a zero or weakly negative dependence of the rate of combustion upon temperature in this region of the pressures. The change in composition frequently acts very specifically, but experimental data are insufficient to make generalizations. Therefore, the thorough study on the temperature dependence of the rate of combustion at low and intermediate pressures would be very useful.

*Effect of the composition of powder
on the rate of combustion*

The rate of combustion of powder at constant temperature pressure depends, in the first place, upon its composition.

The changes in the rate of combustion, depending on the change in its composition, can be caused both by the total effect, which can be connected with the change in the temperature of combustion, and also by the specific effect, which depends on the specific physicochemical action in the definite intermediate stage of combustion.

Muraour [171], on the basis of his numerous investigations, which led to the equation expressing the dependence of the rate of combustion upon pressure

$$u = a/2 + b/2p$$

established that coefficient b (the rate of combustion is expressed in mm/s) is connected with the temperature of combustion by relation

$$\lg(1000b) = 1,214 + 0,3087T_r/1000 \quad (3.29)$$

or

$$\lg b/2 = -2,087 + 0,3087T_r/1000. \quad (3.30)$$

Thus it is proposed that the rate of combustion depends only upon the heat which is liberated during combustion or the temperature attainable by it, but not on the kinetics of the chemical conversion.

These empirical considerations were derived on the basis of data on the rate of the combustions obtained at high pressures. In these conditions the rate of combustion, to a considerable extent, is determined by the transfer of energy from the zone of the flame and, respectively, should depend on the temperature of combustion.

There are no bases, however, to expect, that the indicated dependences will be valid for low and intermediate (below 150 at) pressures, where the flame is either absent or it is located at a considerable distance from the burning surface. In such conditions the rate of combustion of the powder with similar heats of combustion can differ by more than twice. In this region of low pressures the effect of various components can be considerable.

Inasmuch as at very low pressures the rate of combustion, to a considerable extent, is determined by exothermal reactions in the condensed phase, it can be expected that the compositions in which such reactions can be developed will burn in these conditions at a relatively high rate. Powders containing considerable quantities of stabilizing agents, for example, ethylcentralite or diphenylamine, belong to this class and burn stably down to very low pressures. An addition similar to them - *n*-phenylenediamine, is especially active in this respect.

More stable cooling additions, for example, dibutylphthalate or triacetin, do not enter so readily into low-temperature reactions; therefore powders containing these additions are characterized by the limited ability to burn at low pressures. The substances capable of endothermic reaction near the burning surface retard combustion even more greatly. An example of such an addition can be paraformaldehyde. Probably, paraformaldehyde breaks up into formaldehyde and then into monoxide of carbon and hydrogen in zones

of the surface and gives reactions with the absorption of a large quantity of energy. Powder containing 5% paraformaldehyde did not burn at low pressures, but at higher pressures with the approach of the flame to the burning surface the rate of combustion rapidly increased with pressure and approached the magnitude which corresponds to the heat of combustion.

In the region of pressures close to atmospheric [172], the dependence of the rate of combustion of nitroglycerine powder N upon pressure was studied at increased temperatures (Fig. 149). Near the critical pressure the rate rapidly increases with pressure, and, starting from a certain value of the latter, the increase in the rate becomes more gradual and linear. The higher the temperature, the earlier (at lower pressure) the linear section of dependence $u(p)$ becomes. On this section at 85° $u_x = 0,142 + 0,0142 p$; at 115° $u_x = 0,184 + 0,0180 p$. It is interesting that A and B increase with an increase in temperatures at an identical number of times.

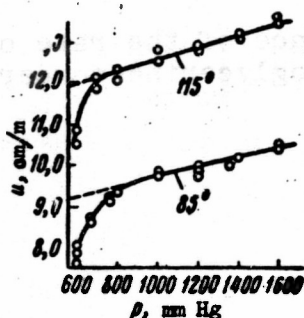


Fig. 149. Dependence of the rate of combustion of nitroglycerine powder upon pressure at increased temperatures.

Powder with a larger content of nitroglycerine was able to burn in these conditions, starting from a lower temperature; term A was for it somewhat less and B considerably more, and the rate of combustion was more respectively.

The ability of powders to burn increases also with the content in them of stabilizing agents of chemical stability. At low temperatures these substances, which are usually weakly basic aromatic compounds, connect the nitric oxides which are formed during spontaneous dissociation of nitroesters. At higher temperatures,

which take place in a heated layer during combustion, the stabilizing agents can react directly with the nitroesters with heat liberation. Therefore, the ability to burn increases. In defined conditions of an experiment, the powder with a large content of the stabilizing agent burned at 35°C at atmospheric pressure, while without a stabilizing agent combustion was observed only starting from 14 at.

The combustion of powder N was studied in the wide interval of pressures and at the usual temperature. At low pressures (down to 4 at) there is observed also a relatively rapid increase in rate,¹ which at high pressures (4-8 at) slows down; however, then the rate again starts to increase more rapidly. Between 8 and 100 at the dependence $u(p)$ can be expressed (Fig. 150) by the relation $u = A + Bp^v$, where v for powder N is equal to 0.84. A similar dependence is given by powder with a large content of nitroglycerine (43%), although, apparently, for it v remains somewhat less than 1 at pressures exceeding 100 at [116].

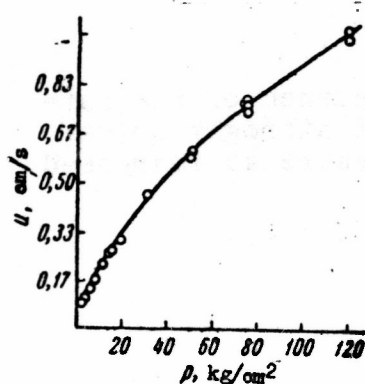


Fig. 150. Dependence of the rate of combustion of nitroglycerine powder upon pressure.

Glazkova [118] determined the rate of the combustion of powder N at constant pressure in an atmosphere of nitrogen in the interval of pressures from 12 to 1000 at. For the experiments small cylinders of powder with a diameter of 5 or 9 mm, coated on the side surface

¹In order to include the region of pressures below 5 at, besides charges with a diameter of 5 mm, which were used for the basic part of experiments, charges with a diameter of 10 and 20 mm were also used.

by perchlorvinyl lacquer were used.¹ Up to 50 at the dependence of the rate of combustion upon pressure can be expressed by the relation

$$u_n = 0,12 + 0,0158 p^{0,33}, \quad (3.31)$$

and in the interval of 50-1000 at the rate increases more slowly and linearly:

$$u_n = 0,62 + 0,00926 p. \quad (3.32)$$

Jacques and James Basset determined the rate of the combustion of a number of powders in an atmosphere of an inert gas in an even wider interval of pressures: from 50 to 10,000 at. The rate was calculated for the interval of time which is required for the breaking of two lead wires with a diameter of 0.1 mm, passed through a column ($d = 3.5$ mm) of powder armored by schellac at a distance of 40 mm from each other. The compositions of the studied powder are given in Table 25, and the dependence of the rate of combustion upon pressure is represented in Fig. 151. Above 1000 at the rate of combustion of all powders increases linearly with the increase in pressure; below 1000 at the curves have a convexity very slight for powder No. 5, more apparent for Nos. 1, 2, 3 and 4 and very greatly expressed for the mixing powder, the rate of the combustion of which in the considerable interval of pressures almost does not change [173].

Table 25. Composition of powders (in %) used in the work of Jacques and James Basset.

No. of the powder	Nitrogen	Nitro-cellulose	Nitro-glycerine	Centralite	Diphenyl-uretan
1	13,04	59,2	31,2	3	6,6
2	12,30	69,7	22	8,55	—
3	14,21	58,7	36,5	4,8	—
4	14,77	58	41	0,99	—
5	11,73	66	21	13,1	—
6	Perchlorate powder				

¹Distinctions in the rate of combustion with these diameters were not observed.

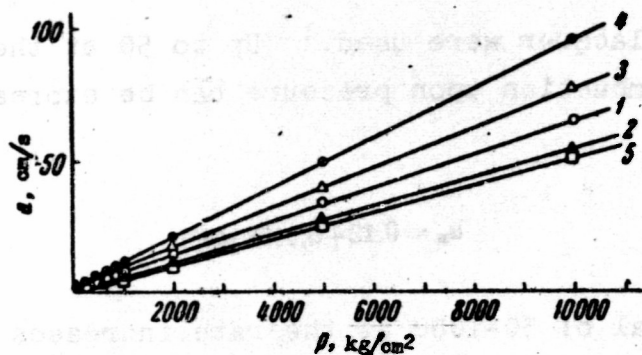


Fig. 151. Dependence of the rate of combustion of the powders studied by Jacques and James Basset, upon press pressure. Numbers near the curves - number of the powder.

An analysis of results of experiments of Basset from the point of view of their conformity to the equation of Muraour and Oney [Translator's note: name not verified], which connects the rate of the combustion of powder at 1000 at with the rated temperature of the combustion, and also some experimental data on the combustion of a number of powders in a bomb of constant pressure in the interval of 40-600 at are given in the article of Muraour and Fauveau [174].

8. Black Powder

By omitting old works on the establishment of the dependence of the rate of combustion of black powder upon pressure [175], investigations on the combustion of tubular powders in fuses [176] and results of experiments on the determination of the rate of combustion of mixtures of black powder with nitroglycerine [126], let us discuss a number of the last investigations on the given problem.

The dependence of the rate of the combustion of black powder (KNO_3 - 78%, S - 10%, carbon - 12%) in the form of a Bickford fuse upon pressure (0.17-30 at) was determined in a bomb of constant pressure [177]. This dependence can be expressed by the relation

$u = Bp^v$, but the values of the coefficients of the equation are different in the different intervals of pressures. For a white fuse at a pressure up to 2 at $B = 0.848$ and $v = 0.528$; above 4 at $B = 1.21$, $v = 2.238$.

Belyayev and Maznev [178], in experiments with pressed ($\rho = 1.75 \text{ g/cm}^3$) columns of powder (KNO_3 - 75%, S - 10%, carbon - 15%) with the thin coating of the side surface for the providing of end combustion, also obtained a more rapid increase in the rate of combustion ($u = 0.88 p^{0.5}$) in the region of pressures up to 5 at than at high pressures; from 5 to 125 at they express this increase by the equation $u = A + Bp^v$, where $A = 1.5$; $B = 0.2$ and $v = 0.47$.

Simultaneously, but in a greater range of the pressures (from 1 to 1000 at), the rate of the combustion of black powder, pressed to great density into small Plexiglass tubes with an internal diameter of 7 mm, was determined by Glazkova [118]. In the interval of 10-1000 at the rate can be expressed by equation $u_m = 2.30 p^{0.216}$. In the region of pressures studied by Belyayev and Maznev, the equations of Belyayev and Glazkova give similar results; however, at high pressures the divergence between the equation of Belyayev and the experimental values of the rate becomes considerable, which indicates the limitedness of the region of its application in the wide interval of pressures.

It is interesting to note that still Vieille [111], on the basis of experiments in a manometric bomb, concluded that the average rate of combustion of maximally condensed black powder in experiments at which the maximum pressure was changed from 1000 to 3000 at is proportional to the pressure to the power of 1/4.

Belyayev also studied the dependence $u(p)$ for "sulphur-free" powder (KNO_3 - 85%, carbon - 15%). In the whole range of pressures up to 125 at the rate of combustion increases considerably less according to expression $u = 0.195 p^{0.5}$.

In an even greater interval of pressures (up to 4000 at), by the method of foliated charges in a manometric bomb, the dependence $u(p)$ for black powder is determined by Belyayev and collaborators [120]. In the region of pressures from 5 to 2000 at the rate increases according to the law $u = Bp^{\nu}$ in accordance with results of works [118, 177], from 2000 to 4000 at the rate remains constant (~ 6 cm/s). In Fig. 152 results of all the mentioned works are compared.

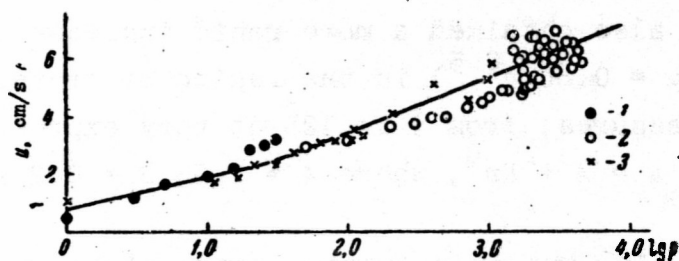


Fig. 152. Dependence of the rate of the combustion of black powder upon pressure according to data of different investigators: 1 - data of Andreyev (for a Bickford fuse); 2 - data of Belyayev (in a manometric bomb with a density of the specimen at 1.76 g/cm³); 3 - data of Glazkova (in a bomb of constant pressure the specimens are pressed into plexiglass tubes up to a density of 1.8-1.9 g/cm³).

The sharp distinction of black powder from secondary explosives with respect to dependence $u(p)$ is not surprising. The combustion of black powder by its mechanism, doubtlessly, is distinguished from the combustions of secondary explosives. This can be concluded if only from the fact that the rate of its combustion at atmospheric pressure is approximately 60 times more than the rate of combustion, for example, of trotyl, which similar to black powder with respect to the heat of combustion. It is possible that the weak dependence of the rate of combustion upon pressure is conditioned by the fact that exothermal reactions with the combustion of black powder occur, to a considerable extent, in the condensed phase, their rate does not depend on pressure, and the transfer of the heat of combustion to the nonreacted substance also goes not only through the layer of vapors or the gases, as during the combustion of secondary explosives, but directly from the solid or liquid products

of the reaction. Furthermore, the conversion of each of the components of black powder with heating occurs with the absorption of heat; heat is liberated only during the interaction of the components or products of their initial conversion, the mixing of which is impeded with an increase in pressure.

According to data of Baum [176], quantity v in the expression for the rate of combustion of tubular powders, other conditions being equal, fact is less, the less the volume of gas products of combustion per unit weight of the powder. Thus, for three powders for which the volume of gases is 515, 330 and 250 l/kg, v has values of 0.607, 0.242 and 0.117 respectively. For compositions which burn without the liberation of gases, the rate of combustion does not depend on pressure.

The relatively slight increase in the rate of combustion with an increase in pressure and decrease in it at high pressures, possibly, are [179] one of the reasons for the low detonation ability of black powder.

9. Thermites

Both the initial and final products of combustion of thermites are products volatilizing with difficulty and also relatively chemically stable substances; the reaction should occur therefore completely or in any case predominantly in the condensed phase. If this is so, then the rate of the reaction, and also, as a rule, and the rate of combustion should not depend on pressure.

Belyayev [180] studied at different pressures up to 150 at the combustion of a number of thermites: chromous aluminum thermite ($\text{Cr}_2\text{O}_3 + \text{Al}$) with a comparatively low temperature of combustion (2000° according to calculation), ferrous aluminum thermite ($\text{Fe}_2\text{O}_3 + \text{Al}$) with a higher rated temperature of combustion, chromous magnesium thermite ($\text{Cr}_2\text{O}_3 + 3\text{Mg}$) and manganese aluminum thermite ($1.5 \text{ MnO}_2 + 2\text{Al}$) (Fig. 153). The thermites were pressed in the form

of cylindrical columns with a diameter of ~ 13 mm up to a relatively low (0.5-0.6) density. The rate of combustion of chromous aluminum thermite (curve 4) practically does not depend on pressure; the rate of combustion of ferrous aluminum thermite (curve 2) increases with pressure in the beginning - up to 40 at - rapidly and then slowly. A unique dependence is given by chromous magnesium thermite (curve 3). At low pressures the rate of combustion increases even somewhat faster than that in ferrous aluminum thermite, at a pressure of 40-50 at the maximum of the rate is reached, and with further increase in pressure the evident drop in rate is observed. At the highest pressures studied combustion becomes pulsating, which, possibly, is connected with the small density of the specimens used. Manganese aluminum thermite (curve 1) behaves similar to ferrous aluminum thermite.

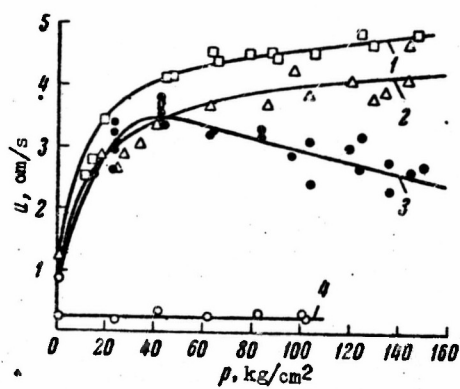


Fig. 153. Dependence of the rate of combustion of thermites upon pressure. 1 - manganese aluminum thermite; 2 - ferrous aluminum; 3 - chromous magnesium; 4 - chromous aluminum thermite.

The independence of the rate of combustion of chromous aluminum thermite of pressure is supposedly caused by the fact that at its low temperature of combustion vapors of the components are not formed and the reaction occurs only in the condensed phase. If this explanation is correct, then one should expect that for other thermites with a lowering of their temperature of combustion, for example, by means of dilution of the thermite by products of combustion, rate should also become independent of pressure.

The gas phase during the combustion of ferrous aluminum thermite should be considered as vaporous aluminum. In view of the insignificant quantity of aluminum being vaporized, the role of the reaction in the gas phase is limited.

IV. Effect of the Initial Temperature on the Rate of Combustion

It is natural to expect that the increase in the initial temperature of the explosives will lead to an increase in the rate of combustion, inasmuch as the entire interval of temperatures through which passes a substance from the beginning of conversion to its end is moved into the region of higher temperatures.

The theory of combustion of Zel'dovich-Frank-Kamenetskiy, proceeding from the assumption that the leading reaction occurs at a temperature equal to the maximum temperature of combustion and examines the effect of the initial temperature on the rate of combustion - the increase in the initial temperature leads to a corresponding increase in the final temperature, in consequence of which expression $e^{-E/RT}$, which determines basically the rate of chemical conversion during combustion, and, consequently, the effect of temperature on its rate, increases.

It is known that for the majority of reactions examined in chemical kinetics, the increase in temperature of 10° increases 2-4 times the rate of the reaction. In the case of combustion the increase in the initial temperature by 10° increases the rate of combustion a total of several percent. This distinction is determined, first of all, by the fact that during combustion the reaction occurs usually at a very high temperature. The increase in the initial temperature by 10° increases the temperature of combustion by approximately the same magnitude; the relative increase in the temperature of combustion is much less than the initial temperature; correspondingly the rate of the reaction at the temperature of combustion increases less.

However, an experiment shows that the reaction which leads to the end product is not necessarily the leading one. This is visually evident in the example of those explosives during the combustion of which a distinctly expressed zonality of reactions is observed, as takes place for nitroglycol and some others nitroesters. When at the sufficient increase in pressure during combustion there starts to occur its concluding stage, which leads to end products of conversion, no increase in the rate of combustion is observed. This fact is not surprising, since the zone of the concluding reaction is located with its appearance far from the surface of the liquid and does not effect processes occurring in it. In this case the leading reaction can be one of the intermediate reactions of the conversion of the substance passing, respectively, at a lower temperature. Then, other conditions being equal, the rate of combustion will more greatly depend on the initial temperature, inasmuch as with its certain increase the increase in temperature of the leading reaction will be relatively more than the increase in the final higher temperature.

Finally, such a case is possible when the temperature and, consequently, the rate of the leading reaction do not depend on the initial temperature. As an example it is possible to show the combustion of a liquid substance at which the leading exothermal reaction occurs in the condensed phase, and the temperature of the latter is limited to the boiling point. Despite the constancy of temperature of the leading reaction and the independence of this temperature of initial temperature, the rate of combustion will depend on the initial temperature, inasmuch as with its increase the quantity of heat which must be imparted to the liquid for its heating to the boiling point will decrease. The critical temperature in the indicated meaning can be not only the boiling point but also the temperature of the intense gasification, which leads to dispersed substance.

The concept about the heating of the substance during combustion up to a certain critical temperature as the basic factor which determines the rate of combustion, is contained in the hypothesis of

Mallard and the Le Chatelier, especially in its application to the combustion of condensed explosives. Incorrect in this hypothesis is basically the identification of the critical temperature with the flash temperature, the physical meaning of which at that time was still not sufficiently clarified. Of course, this hypothesis should not oppose the theory of Zel'dovich-Frank-Kamenetskiy. The realization of a certain mechanism of combustion depends on specific features of the substance. Such a contrast all the more would not be substantiated, inasmuch as Zel'dovich in essence developed the concept on combustion on condition of the occurrence of the leading reaction in the condensed phase, the temperature of which does not depend on the initial temperature, allowing for the kinetics of the heat-releasing reaction, which was not done by Mallard and Le Chatelier.

Such a theory leads to the regularity of the process different from those which are obtained during combustion when the leading reaction occurs at maximum temperature. Both these hypotheses lead, specifically, to different dependences of the rate of combustion upon the initial temperature and also on pressure. An experiment indicates that many, including in practice the most interesting, cases are in better agreement with the conclusions which come from the assumption on the combustion at constant temperature of the leading reaction than with the hypothesis of the gas-phase process.

The dependence of the rate of combustion upon the initial temperature represents a great engineering interest. It is desirable, especially for powders intended for the combustion in a semiclosed volume, that this dependence be a minimum, which provides greater constancy of the equilibrium pressure at different temperatures of an engine.

The determination of the rate of combustion at the temperatures different from the temperature of the environment at increased pressures is complex because it requires thermoregulating those rather bulky instruments (bomb of constant pressure, manometric bomb), which are used for studying combustions at increased pressures, or

placing a thermostat in these instruments. Because of this a large part of the investigations is conducted at atmospheric pressure or pressures close to it.

Measurement of the dependence of the rate of combustion upon a temperature is limited to lower and upper limits of the latter. The lower limit is that minimum temperature below which under the given conditions (diameter of the charge, pressure) combustion is not propagated. The upper limit of temperature in any case is limited by temperatures lying near the flash temperature of the given explosives. However, for some explosives, especially liquid or cellular, the normal flow of combustion is broken at temperatures still far from the flash temperature; in this case combustion can become pulsating, convective, and moving at high speed or can even turn into an explosion.

The dependences of the rate of a combustion examined below upon the temperatures of various explosives belong to those intervals of temperature and of other parameters affecting the stability of combustion in which the normal flow of combustion is not broken.

DEPENDENCE OF THE RATE OF COMBUSTION UPON INITIAL TEMPERATURE AT ATMOSPHERIC PRESSURE AND PRESSURES CLOSE TO IT

1. Nitroesters and Nitrocompounds [81, 114, 181]

The dependence of the rate of combustion of methyl nitrate upon temperature was studied within the limits of 0 to 53°C (Fig. 154); at 60°C after the short section of combustion there appears an explosion.

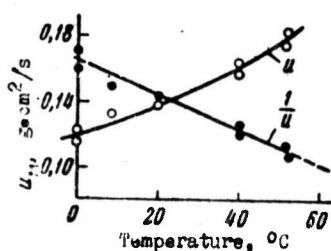


Fig. 154. Dependence of the rate of combustion of methyl nitrate upon initial temperature.

Nitroglycol in tubes of small diameter burns even at -20°C . The rate of its combustion is considerably less than that of methyl nitrate. In a number of works the rate of combustion at atmospheric pressure was measured in the interval of temperatures from 0° to almost the boiling point ($\sim 200^{\circ}\text{C}$) (Fig. 155). Near the boiling point the increase in the rate is intensified and reaches 1-5 cm/s, which is connected with the formation of bubbles as a result of decomposition, liberation of dissolved air and of vapor formation. The rate of combustion of nitroglycol, gelatinized by 3% colloxylin was measured also; at room temperature it is less than that of nongelatinized liquid but increases with temperature more rapidly and, at 100°C the rates are almost identical.

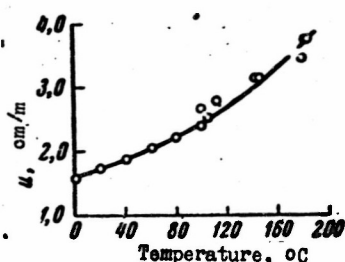


Fig. 155. Dependence of the rate of combustion of nitroglycol upon initial temperature.

Diethelene glycol dinitrate burns even more slowly than does nitroglycol and only with large diameters of the charge. The dependence of the rate of combustion of the liquid and gelatinized substance upon temperature is similar to that established for nitroglycol (Fig. 156).

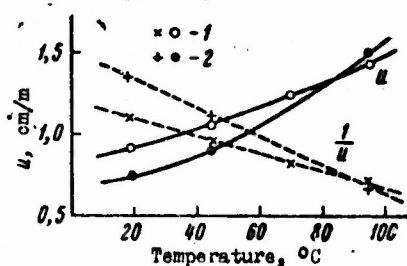


Fig. 156. Dependence of the rate of combustion of liquid and gelatinized diethylene glycol dinitrate upon initial temperature. 1 - liquid; 2 - gelatin.

For liquid nitroglycerine systematic experiments on the determination of the dependence of the rate of combustion upon temperature were not carried out. It burns at 20° and 300 mm at the rate of 0.068 cm/s, and at 98° it increases up to 0.117 cm/s, i.e., (1.7 times) noticeably more greatly than that for liquid nitroglycol (at atmospheric pressure - 1.4 times). Gelatinized (97:3) nitroglycerine burns at the rate of approximately 4 times greater than that of nitroglycol and rises more rapidly growing with temperature (Fig. 157).

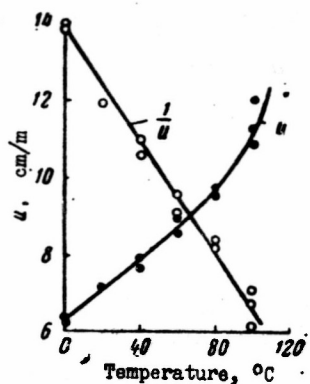


Fig. 157. Dependence of the rate of combustion of gelatinized nitroglycerine (97:3) upon initial temperature.

The combustion of solutions of nitroesters depending on the relationship of components was also studied. The rate of combustion of a solution of nitroglycol in nitroglycerine at room temperature increases with an increase in the nitroglycerine content, not additively but more slowly (Fig. 158). At 50-60% nitroglycerine after the short section of combustion (5-7 mm), there approaches a extinguishment, and at 75% nitroglycerine the solution does not burn but gives with ignition a flash with a spatter, similar to that which is observed in experiments on pure nitroglycerine. The rate of combustion with extinguishment by extrapolation is about $0.09 \text{ g/cm}^2\text{s}$, i.e., it exceeds only 2 times the rate of combustion of the nitroglycol.

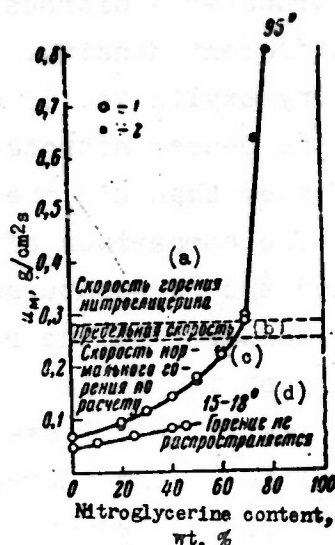


Fig. 158. Dependence of the rate of combustion of solutions of nitroglycerine upon initial temperature. 1 - normal combustion; 2 - pulsating combustion.

KEY: (a) Rate of combustion of nitroglycerine; (b) Maximum rate; (c) Rate of normal combustion according to calculation; (d) Combustion is not propagated.

At higher temperature (95%) the rate of combustion of the solution increases with an increase in the nitroglycerine content more rapidly than it does at a room temperature, i.e., the temperature coefficient of the rate of combustion also increases with an increase in nitroglycerine content. In this case even mixtures with a considerably greater content of nitroglycerine (up to 70%) are to burn. The rate of combustion of a 70% solution is comparatively great and consists of $0.29 \text{ g/cm}^2\text{s}$. At large contents of nitroglycerine combustion occurs with powerful pulsation (sometimes extinguishing), and the average rate sharply increases.

Diglycoldinitrate + nitroglycerine. At room temperature the combustion of solutions of these nitroesters in tubes with an internal diameter of 6 mm is extinguished without reaching to the end of the column of the liquid. At increased temperatures (92-97°C) pure diglycoldinitrate in tubes of the same diameter burns at the rate of 0.022 cm/s. With an increase in the nitroglycerine content the rate of combustion increases, at a content of 60% nitroglycerine it is 0.09 cm/s, at 70% - 0.14 cm/s, and at 80% nitroglycerine in a mixture with ignition there is a flash typical for nitroglycerine with a spatter of the liquid, and combustion is not propagated.

The rate of combustion of nonvolatile nitroester - nitrocellulose - was studied depending on the temperature at different density. At 0° the rates of combustion of nitrocellulose (pyroxylin No. 1) at different density were identical, and at 95° the denser nitrocellulose ($\rho = 0.6-0.7 \text{ g/cm}^3$) burned almost 1.5 times faster than did the less dense nitrocellulose ($0.19-0.26 \text{ g/cm}^3$). The comparison of the rate of combustion at different density and two temperatures (18 and 95°C) is given in Fig. 159. At a low temperature the rate of combustion does not depend on density in almost its whole studied interval. On the contrary, at 95°C a distinct increase in the rate is observed both at low and high densities. The increase in the rate at low density is conditioned by a trivial reason - by the penetration of gases into the depth of the powder, taking place for the given specimen of pyroxylin when $\rho = 0.2 \text{ g/cm}^3$. At an increased temperature this penetration occurs more easily than at low. The increase in the rate at high densities probably is connected with the increase in the thermal conductivity of nitrocellulose with an increase in density. For the horizontal part of the curve, the temperature coefficient of the rate of combustion is 1.97. With an increase in density above 0.6 it becomes even more.

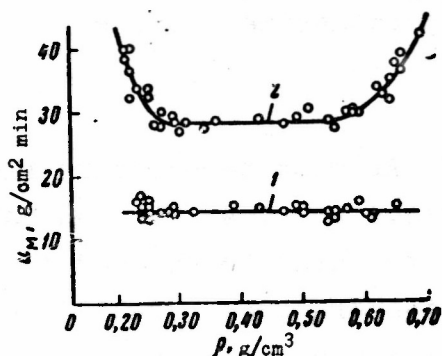


Fig. 159. Dependence of the rate of combustion of pyroxylin No. 1 upon density at various temperatures. 1 - at 18°C; 2 - at 95°C.

From nitro compounds were studied hexogen, tetryl and trotyl (Figs. 160, 161 and 162). The rate of the combustion of trotyl very slowly increases with temperature and only at temperatures above 250°C (in glass tubes) is there observed considerable acceleration of the combustion. However, this acceleration approaches not immediately after the beginning of the combustion but only after it

passes a certain path and is accompanied by pulsation and ejection of sprays of burning liquid. Apparently, this is connected with the heating and decomposition of the liquid as a result of the transfer of heat on walls of the tube. In copper tubes, according to their greater thermal conductivity, pulsation approaches at lower temperatures and the earlier it does, the higher the temperature of the experiment.

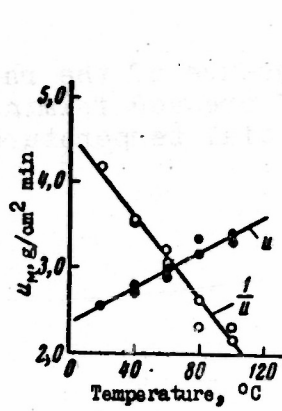


Fig. 160.

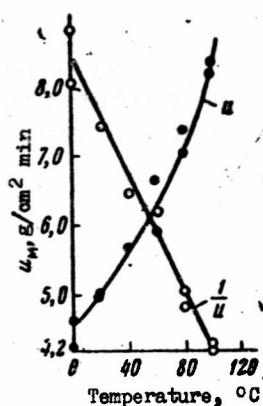


Fig. 161.

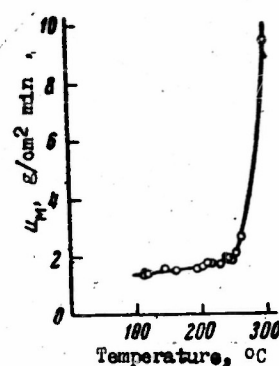


Fig. 162.

Fig. 160. Dependence of the rate of combustion of hexogen upon initial temperature.

Fig. 161. Dependence of the rate of combustion of tetryl upon initial temperature.

Fig. 162. Dependence of the rate of combustion of trotyl upon initial temperature.

2. Priming Explosives

The dependence of the rate of combustion of pressed fulminating mercury upon temperature was determined at different pressures lower than atmospheric [182]. The obtained data with corrections on the dynamic increase in pressure are given in Fig. 163. The rate of combustion increases with temperature not linearly but somewhat more rapidly. With the increase in temperature by 100°C the rate of combustion increases approximately 1.7 times, close to that

which is observed for many secondary explosives. Figure 164 shows also the dependence of the rate of combustion upon pressure at different initial temperatures. At all temperatures this dependence is linear. In this case, the straight lines continue to the left, then they all will intersect with the axis of the abscissas at one point. At 20°C $u = 0.47 + 1.05 p$; at 90°C $u = 0.65 + 1.44 p$ and at 105°C $u = 0.71 + 160 p$. Ratio $A:B$ at all temperatures is constant, i.e., A and B are changed equally with a change in temperature.

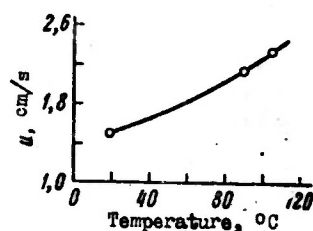


Fig. 163. Dependence of the rate of combustion of pressed fulminating mercury upon initial temperature.

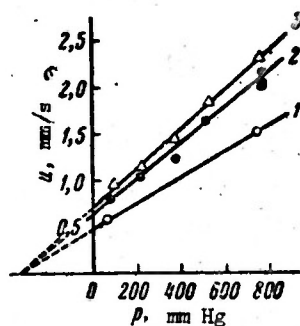


Fig. 164. Dependence of the rate of combustion of fulminating mercury upon pressure at different initial temperatures (in °C): 1 - 20; 2 - 90; 3 - 105.

There were also conducted experiments in which the time of the preliminary heating of the pellet of fulminating mercury was increased. Figure 164 shows by a solid square the average value of the rate corresponding to the preliminary heating at 90°C in 1 hour instead of 15 minutes. Longer heating led to a certain lowering of the rate of combustion, which is retained even upon cooling at room temperature.

The described results of the experiments of Belyayev somewhat disagree with the data of Muraour and Wolgemuth [183], who with the ignition of the pressed fulminating mercury at 108°C, and all the more at 120°C, observed an apparent mechanical action on the lead liner; heating at 130°C led to spontaneous ignition, which had the nature of an explosion with a very powerful effect on the liner.

In experiments of Belyayev [184] at these temperatures only sometimes did an explosion appear and usually an unstable combustion took place with passage of the flame along the surface at the rate of 2.5-3.5 cm/s but without mechanical action. It is possible that this distinction is connected with the distinction in the dimensions of the pellets or modes of heating, which were used in both works. In any case the considerable variations of the rate from an experiment to experiment indicated that combustion is located on the limit of stability and is completely inclined to acceleration and transition into an explosion.

3. Powder

A number of works, conducted with armored charges of powder N [114, 185, 186], in the interval of temperatures from -18° to 125°C in somewhat different conditions, gave the dependence of the rate of combustion upon temperature given in Fig. 165 and 166. Attention is given to the great and pronounced increase in the temperature coefficient of the rate of combustion of powder occurring at a temperature of about 20°C.

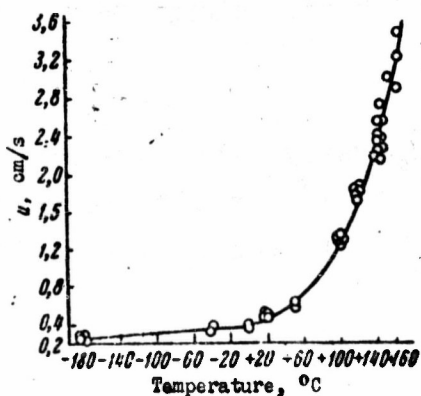


Fig. 165. Dependence of the rate of combustion of powder upon temperature.

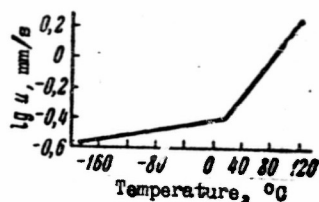


Fig. 166. Dependence of the rate of combustion of powder upon temperature in coordinates $\lg u-T$.

In somewhat other conditions [187] and in the narrow interval of temperatures (75-130°C) the rate of combustion of various nitroglycerine powders was determined by Muraour and Schumacher. An especially pronounced acceleration of combustion is observed near 130°C, probably, as a result of the exothermal reaction of the decomposition of the powder occurring at this temperature, which increases the temperature and changes the structure of the powder.

All these data are obtained at atmospheric pressure; they indicate the great increase of the rate of combustion with the increase in temperature. At increased pressures the temperature coefficient of the rate of combustion falls, approaching a certain constant.

Thus, if at 1 at the rate of combustion of nitroglycerine powder N with an increase in temperature from 15° to 95° increases 2.45 times, then at 2 at it increases only into 2.07 times, and at 20 at - only 1.7 times with a change in temperature from -60° to +60°. Further increase in pressure does not change the temperature coefficient in the region of positive temperatures.

According to data of Baum [176], the rate of combustion of tubular powder weakly depends on temperature, and with its change from -30 to +44° the rate increases by only 5%.

According to experiments of A. A. Shidlovskiy, the rate of combustion of pressed black powder ($\rho = 1.7 \text{ g/cm}^3$) at 13° and 95°C was respectively, 0.95 and 1.04 cm/s, i.e., it increased by only 15%.

The same temperature coefficient was obtained by Belyayev and Lukawenya [188] in the interval of temperatures of 20-250°C. Thus, the rate of the combustion of black powder in comparison with the other explosives studied very weakly depends on temperature. It is interesting, however, that with an increase in pressure up to 10 at the temperature coefficient of the rate of the combustion of black powder, according to data of Belyayev, does not decrease, as is observed for other explosives, but greatly (two times) increases.¹ The temperature coefficient for "sulfur-free" powder (KNO_3 - 85%, carbon - 15%) is greater, than usual ($5 \cdot 10^{-3}$ 1/deg); with an increase in pressure (up to 10 at) it is lowered to $3 \cdot 10^{-3}$ 1/deg.

¹This, by the way, means that the dependence of the rate of combustion of black powder upon pressure at high temperatures becomes greater.

DEPENDENCE OF THE RATE OF COMBUSTION UPON TEMPERATURE AT INCREASED PRESSURES

A considerable difficulty in the photographic determination of the rate of combustion at increased temperatures and pressures consists in the fact that because of amplified convection with the small dimensions of the thermostat it is difficult to maintain the constancy of temperature in the specimen over its entire height and during the whole time of combustion. These difficulties were surmounting; a thermostat was designed in the form of a thermally insulated red copper block of a square section (35×35 mm) 120 mm in height with a central channel and windows closed with glass. An [VV] (BB) explosive was placed in the plexiglass tube, which eliminated the possibility of the advanced heating of the charge during combustion by a thermal wave propagating along the walls of the tube and also as a result of the possible increase in temperature of the thermostat because of heating by its heat liberated during combustion. The transparency of the tube allowed the recording of rate and the nature of combustion photographically, the application of the plexiglass tube made it possible to press the explosive to great compactness. The total error of the measurement did not exceed $\pm 4\%$. For arrangements of the instrument and the procedure of the experiment see in detail works [122, 189].

The dependence of the rate of combustion upon temperature in the interval from 20° and up to the upper limit ($110-200^\circ$ for different explosives) was determined at pressures of 1 to 50 at.

The rate of combustion all the studied explosives nitrocellulose, PETN diglycoldinitrate, tetryl, hexogen, trinitrobenzene, diaminotrinitrobenzene, hexanitrodiphenylamine increases with an increase in temperature. The rates of this increase are substantially different for different explosives (Fig. 167) and also depend upon pressure, decreasing with an increase in pressure (Fig. 168).

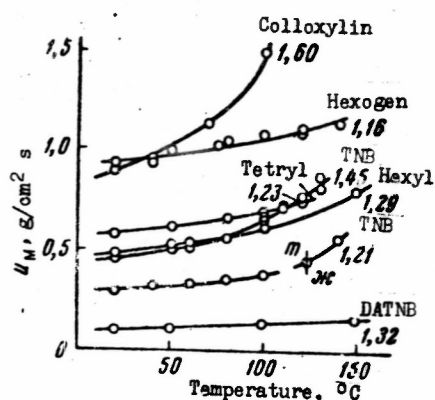


Fig. 167.

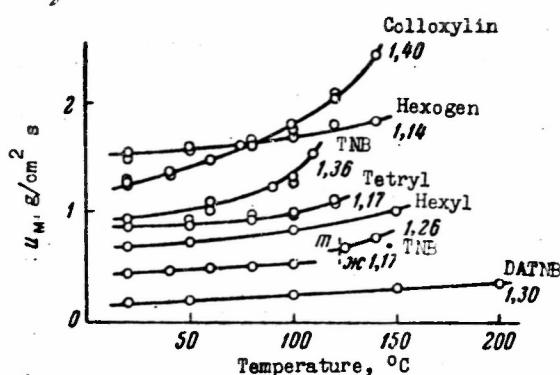


Fig. 168.

Fig. 167. Dependence of the rate of combustion of secondary explosives upon temperature at 25 at. Numbers near curves - K_1 (see Table 26): m - solid TNB; ж - liquid.

Fig. 168. Dependence of the rate of combustion of secondary explosives upon temperature at 50 at. Numbers near the curves have the same values as those in Fig. 167.

Table 26 gives temperature coefficients of the rate of combustion of explosives studied at different pressures. The rate of combustion of nitroesters - nitrocellulose, diglycoldinitiate and PETN increases the greatest with temperature; the least increase is observed in hexogen, trinitrobenzene and tetryl; the remaining explosives occupy an intermediate position.

Table 26. Temperature coefficients $K_1 = u_{100^\circ}/u_{20^\circ}$ of the rate of combustion of secondary explosives at different pressures.

Explosives	Pressure, at								
	1	5	10	12	20	25	30	40	50
Hexogen.....	1,25	1,19	1,17			1,16			1,14
PETN.....					1,51	1,45		1,40	1,36
Tetryl.....				1,35		1,23	1,20		1,17
TMB.....						1,21			1,17
DATNB.....						1,32			1,30
Hexyl.....						1,29			1,26
EGDN.....						1,63			
Pyroxylin No. 1.....					1,57			1,33	
Colloxylin.....	1,98					1,60			1,40

The temperature coefficient for the majority of the explosives studied increases with an increase in temperature (Fig. 169). This dependence is more greatly expressed in nitrocellulose and less in hexogen; it decreases with an increase in pressure, if for some explosives the region of high temperatures is excluded (Figs. 170 and 171).

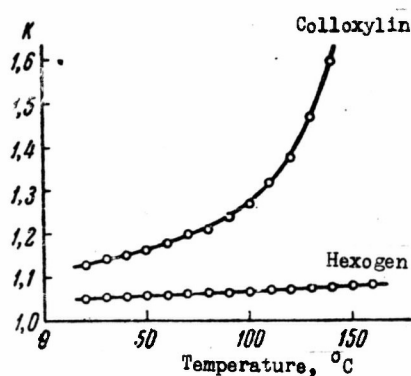


Fig. 169.

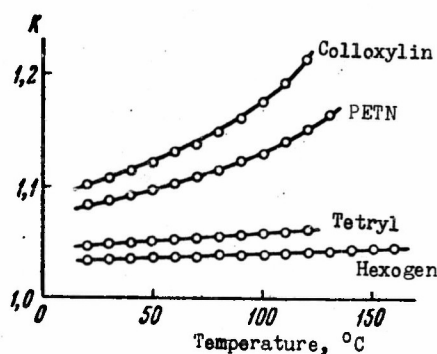


Fig. 170.

Fig. 169. Dependence of the temperature coefficient of the rate of combustion of colloxylin and hexogen upon temperature at 1 at ($k = u_{t+10}/u_{t-10}$).

Fig. 170. Dependence of the temperature coefficient of the rate of combustion of secondary explosives upon temperature at 25 at ($k = u_{t+10}/u_{t-10}$).

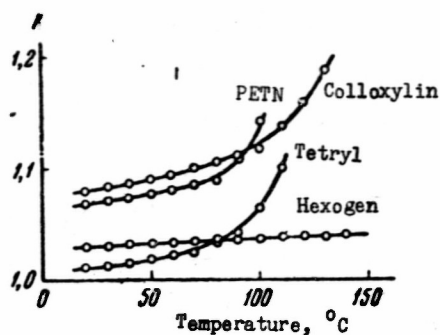


Fig. 171. Dependence of the temperature coefficient of the rate of combustion of secondary explosives upon temperature at 50 at ($k = u_{t+10}/u_{t-10}$).

For two explosives - trinitrobenzene and tetryl - the melting point lies in the interval of temperatures studied. In the transition from a solid state to a liquid the rate of combustion increases: this change, which increases the interval energy of the explosive on the heat of fusion, is equivalent to the increase in temperature of trinitrobenzene by ~ 70 and tetryl to 90°C . Despite the approximately identical increase in enthalpy (and rated temperature), the rate of combustion of tetryl especially greatly (approximately 10 times) increases at 25 and 50 at (Fig. 172), and much more weakly (20-30%) in the same conditions the rate of combustion of trinitrobenzene increases. In the latter case combustion occurs in the pulsating mode, which still does not lead, however, to a high rate of combustion; tetryl, obviously, burns in a stable rapid microturbulent mode (inasmuch as nonuniformity of combustion is not observed) which is accompanied, probably, by the dispersion of the substance.

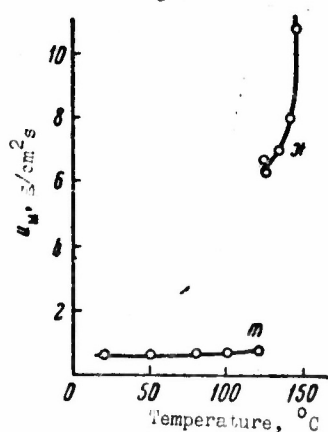


Fig. 172. Dependence of the rate of combustion of tetryl upon temperature in the interval of 20-160°C at 25 at m - solid tetryl; m - liquid.

It is possible that connected with the instability of the normal mode of combustion of fusion is and the aforementioned sudden acceleration of combustion of PETN and tetryl at high initial temperatures and pressures. With an increase in the initial temperature the depth of the heated layer, specifically, its molten part increases. If the bed of the melt is thin, then turbulization is not developed in it. This follows from the fact, that at the usual temperature the solid but melting explosives burn many times more slowly than in a liquid state in conditions when the turbulent mode of combustion is carried out. If a molten layer becomes quite thick, then the agitation can be developed, and combustion is accelerated.¹ The development of these processes can be furthered also by the decrease in the melting point as a result of the accumulation of condensed products of dissociation in the heated layer.

Finally, with combustion under increased pressures the concentration in the condensed phase of gas products of decomposition, becomes great, which, as is known, greatly accelerate, for example, thermal dissociation of PETN.

In experiments at increased temperatures the combustion individual explosives differs in some features. Thus, for hexogen and PETN the bifurcation of the flame into initial and secondary is observed. In the determination of $u(t)$ for diglycoldinitrate at 25 at and 150°, and also at 5 at and 120° powerful explosions occurred; at 100° in several experiments the extinguishment of the combustion was observed after the burning out of a certain section. Apparently, these phenomena are connected with the transition in combustion of the liquid into a turbulent mode.

¹This explains, probably, the fact that, starting from a certain temperature, the ignition of PETN leads not to stationary combustion, but to a flash; with the ignition the flash appears at less temperature and higher pressure (starting from 130° at 25 at and from 110°C at 50 at).

The decrease in the temperature dependence of the rate of a combustion with an increase in pressure was observed not only in individual explosives, but also in ballistite powder. Figure 173 gives the dependence of the temperature coefficient of the rate of combustion of nitroglycerine powder with 43% nitroglycerine upon the pressure [116]. In the interval of the temperatures of 25-50°C this coefficient falls with an increase in pressure to 35 at; with a further increase in pressure up to the studied limit (250 at) the temperature coefficient remains constant.

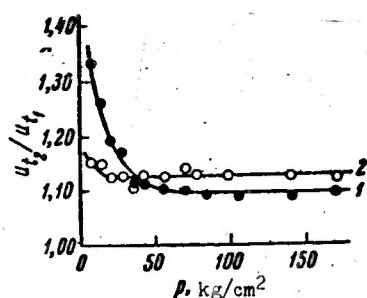


Fig. 173. Dependence of the temperature coefficient of the rate of combustion of nitroglycerine powder upon pressure. 1 — u_{25}/u_{50} ; 2 — u_{25}/u_{50} .

The temperature coefficient of the rate of combustion undergoes a similar change in the interval of temperatures from 25° to 0°; the distinction consists only in the fact that the constant value of the temperature coefficient is reached at a higher pressure (50-60 at).

The rate of combustion of nitroglycerine powder at different temperatures (-80°, +18° and +97°C) was determined also at even higher pressures in a manometric bomb, i.e., during combustion under increasing pressure [190]. Accepted as its characteristic was the reciprocal $\int p dt$. Experiments indicated that $1/\int p dt$ increases with an increase in temperature from -80° to +97°C 1.7 times.

Conclusions

The rate of combustion all the explosives studied increases with temperature.¹ This increase is small. Table 26 gives for a number of explosives values of the temperature coefficient – relative magnitude of the increase in the rate of combustion with an increase in temperature by 1°C.

With an increase in the initial temperature by 100°C the rate of combustion at atmospheric pressure increases, as a rule, by 30-100%. Generally speaking, the known conformity is observed between the temperature coefficient of the rate of combustion at atmospheric pressure and temperature of the flash. The higher the temperature of the flash (trotyl, black powder), the less the rate of combustion depends upon temperature.

For many explosives the temperature coefficient of the rate of combustion is not constant but increases with the temperature, and for some explosives (hexogen) it is weaker and for others (nitrocellulose, PETN) considerably stronger.

The dependence of the rate of combustion upon the initial temperature can be expressed in its considerable interval by straight lines in coordinates $\frac{1}{v}-T$ in accordance with the semiempirical relation $\frac{1}{v} = A_1 - B_1 T_0$. From this expression it follows, specifically, that the temperature coefficient $K = \frac{B_1}{A_1 - B_1 T_0}$ increases with temperature. Quantitatively this increase depend on the relationship between constants A_1 and B_1 and also on T_0 ; in the region of low temperatures it is little, and with an increase in temperature it increases.

¹In literature there are nonspecified references to the fact that for some powders in the definite interval of temperatures the rate of combustion with an increase in temperature decreases.

The temperature coefficient, as a rule, decreases with an increase in pressure. In the region of low pressures this decrease occurs faster than with high pressures. It is possible, therefore, that with a sufficient increase in pressure the temperature coefficient is lowered down to a certain constant value, as was observed for nitroglycerine powder with 43% nitroglycerine studied in a relatively large interval of pressures.

A certain parallelism is also observed between the change with pressure of the temperature coefficient and the relative heat of combustion (the ratio of actual heat to the highest possible). If the relative heat of combustion is great at atmospheric pressure (hexogen), then the temperature coefficient is small and weakly decreases with pressure; if it is small (nitrocellulose), then the temperature coefficient is great and is decreased more strongly with an increase in pressure.

The temperature coefficient of the rate of combustion of liquid explosives depends, apparently, also upon their physical features and upon the change in these features with the change in temperature.

The temperature coefficient of the rate of combustion of nitrocellulose depend on the relative density, and at high densities it increases, probably, because of the reaction in the condensed phase, which leads to the increase in the rate of combustion at increased temperatures.

V. The Effect of Relative Density, Diameter of the Charge and Inert Admixtures on the Possibility and Rate of Combustion

The effect of the relative density of powdery explosives on the possibility and rate of combustion represents considerable interest according to the following considerations [191].

The change in relative density, obviously, cannot affect the rate of the chemical reactions occurring in a gas phase. It also cannot have a direct effect on the flow of reaction in a condensed phase. At the same time the conditions of the propagation of heat in a condensed phase can be substantially changed both as a result of the change in thermal conductivity of the powder and as a result of the change in its penetrability for the material heat carriers - liquid (melt of the substance) or gas (gas products of vaporization and dissociation). Thus, the study of the effect of relative density on combustion allows the revealing of the role of the propagation of heat in the condensed phase in processes of combustion. The change in conditions of the propagation of heat in powder explains the unique effect of the relative density on the possibility and rate of combustion of various solid explosives.

This effect was studied on two melting powdery explosives - tetryl and hexogen and two infusible ones - nitrocellulose and nitroglycerine powder pulverized into powder.¹

1. Effect of Relative Density of Explosives on the Possibility of Combustion

Experiments indicated that for melting explosives there exists a minimum limit of relative density near which the combustion, uniform at higher densities, becomes pulsating but at lower is extinguished. The maximum density depends on the diameter of the tube: with a greater diameter it is less. It depends also upon dimensions of crystals of explosives. Experiments on the clarification of the effect of dimensions of crystals of a substance [192] were conducted with three specimens of tetryl; the first specimen represented relatively large crystals, which were passed

¹Nitroglycerine powder is considerably softened with heating up to high temperatures, but it retains quite high viscosity and behaves in conditions of combustion as an infusible substance.

through sieve No. 49² and remained on sieve No. 73, the second specimen - crystals of average dimensions, which were passed through sieve No. 73, and the third specimen the smallest crystals obtained by the pulverizing of tetryl in mortar. Combustion was produced in glass tubes with an internal diameter of 19 mm.

Results of experiments given on the diagram of Fig. 174 indicate that the larger the crystals, the more the lower limit of density. In this case the mass rate of combustion near the limit depends on dimensions of the crystals: with large crystals is clearly more.

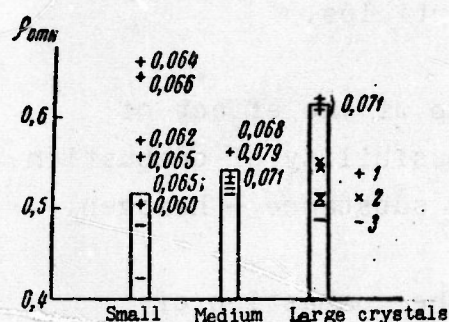


Fig. 174. Effect on the possibility and rate of combustion of tetryl of relative density and dimensions of particles: 1 - a uniform combustion (numbers on the right indicate the mass rate of combustion in g/cm²s); 2 - non-uniform combustion; 3 - extinguishment.

The reason for the transition in combustions into a pulsating mode and its extinguishment at small densities with the combustion of melting substances consist in too high a rate of removal of heat into the condensed phase. At low densities this removal occurs in a considerable part by means of the penetration of the melt of the substance into intervals between particles. If this penetration is small, then the substance burns, and its rate can even be somewhat higher as a result of the increase in the heat arrival from the products of combustion, which we observe in experiments with

²Dimension of sieve No. 49 - 0.123 mm, sieve No. 73 - 0.084 mm.

large crystals. If, however, as a result of the increase in dimensions of intervals between the particles the penetration of the melt will be extremely eased, then the heat removal into the depth of the charge can become so great that it will not be compensated by the heat arrival from the gases, and combustion is extinguished. Without explanations, the importance with the described mechanism of the effect of dimensions of the crystals and relative density is understandable; the increase in diameter of the charge decreases the losses of heat into the environment and shifts, respectively the maximum values of the other two parameters. Let us add that for the specimens of tetryl with a different form of crystals different values of maximum density were observed, and that it is natural to connect these with distinctions in the penetrability of powder for the fusion, depending not only upon dimensions, but also upon the form of the particles.

Similar observations in the relationship of the effect of density and dimensions of crystals on the possibility of combustion were made and for the second studied melting substance – hexogen.

The effect of the relative density on the combustion of infusible powdery explosives is somewhat distinguished from that described above. At small densities the minimum of density can also be observed,¹ lower than which the uniform combustion gives way to pulsating combustion; however, the reason for the pulsation in this case is different: with a decrease in the resistance of powder as a result of an increase in the intervals between the particles the penetration of gas products of combustion into the depth of the powder starts to play a role. The effective surface of combustion increases, and the quantity of the substance, which burns per unit time increases. Usually the acceleration of combustion in conditions of described experiments was transient and was changed by deceleration, after which followed again acceleration, etc. – combustion was pulsating.

¹This minimum cannot always be detected – it can be less than the filled density.

The reason for the pulsation should be seen in the fact that with the penetration of gases into the depth of the powder the surface of the contact of gases with the particles of powder greatly increases; the gases in this case are highly cooled, and the particles of powder are heated insufficiently to ignite immediately. However, after a certain induction period in the heated layer of the explosives a flash in the form of a rapid combustion occurs. It leads to an increase in pressure, which forces hot gases to penetrate again into considerable depth of the explosives. After the burning of the deflagrated layer the pressure drops, and the rate of combustion also temporarily decreases; then again there occurs a flash of the heated gases of layer and so on.

The drop in pressure, the absence of a heated layer, which burned out, a decrease in temperature of the gases, leading with pulsating combustion to the time periodic deceleration of the process, can lead as well to the extinguishment of combustion, which was observed experimentally with known relationships between dimensions of the particles, their combustibility and conditions of the experiment. If the intensity of the flash of the layer, heated by the penetrating gases, is sufficiently great, then it can lead to an avalanche-like acceleration of the penetration of gases and combustion into the depth of the charge, which finishes with an explosion.

Thus, the behavior at low densities of infusible explosives from the point of view of the possibility of penetration into the powder of the heat carriers (with its appropriate reactions) is similar to melting explosives.¹

¹During the combustion of melting explosives the penetration of gas products of combustion into the depth of the powder at small densities does not occur, since gases are separated from the powder by a layer of fusion.

A considerable distinction between melting and infusible explosives is observed in increased density. For infusible explosives there is a certain upper limit of relative density above which the combustion, other conditions of the experiment being equal, is not propagated. Thus, for instance, in experiments with pyroxylin No. 1 in tubes with an internal diameter of 5-10 mm combustion was extinguished if the density of the powder exceeded $0.5-0.6 \text{ g/cm}^3$. Nitroglycerine powder pulverized into powder stably burned in glass tubes with an internal diameter of 9 mm at a relative density of 0.4, and at a density of about 0.6 combustion was extinguished, not reaching the end of the charge. The charge of powder ($\rho = 1$) does not burn even with a diameter of 15 mm.

The reason for the existence of the upper limit of the relative density in essence is the same as that of its lower limit - the excessive increase in the rate of the propagation of heat in the condensed phase. At greater densities of the powder its thermal conductivity increases so that the heat is removed into the depth of the substance more rapidly than it is fed from the gas phase, and because of this combustion is extinguished.

It would seem that such an effect should appear even during the combustion of melting substances. However, the state of the zone of the increased temperature - the zone of fusion - and its thickness at great densities here practically do not depend on density; they do not depend, therefore, upon the latter and the heat loss of the heated layer of the condensed phase. Therefore, the upper limit of the relative density for melting explosives is not observed.

2. Effect of the Relative Density of Explosives on the Rate of Combustion

The change of relative density is not directly reflected on the course of reactions in the gas phase and heat transfer from gases of the condensed phase. However, since the heat capacity of a unit of volume of a substance is directly proportional to the

relative density, then the volume of the substance heated by the gases to a certain definite temperature per unit time with a decrease in density respectively increases. Therefore, the linear rate of combustion should increase with a decrease in relative density. Experiments confirmed that with the change in relative density of the powder the linear rate of combustion is changed.

For a number of studied powdery explosives (tetryl, hexogen, nitrocellulose, powder of nitroglycerine powder) the magnitude of the linear rate of combustion is approximately inversely proportional to the relative density, and the product of these magnitudes, i.e., the mass rate of combustion, is approximately constant [192]. For tetryl this was established in the interval of relative density from 0.4 to 0.6 g/cm³, for hexogen - from 0.38 to 0.64, for nitrocellulose - from 0.12 to 0.36, for powder - from 0.37 to 1.

Figure 175 gives experimental results for individual explosives. From the graph it is evident that the constancy of the rate is not strict. In the case of tetryl, hexogen and gunpowder the mass rate somewhat increases with an increase in density.

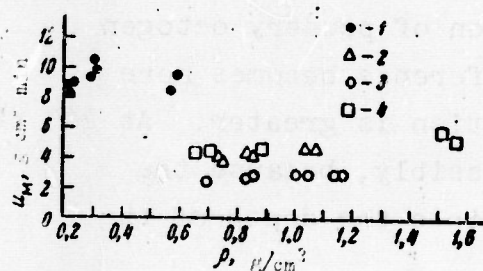


Fig. 175. Dependence of the combustion of some explosives upon cubic density. 1 - pyroxylin No. 1; 2 - tetryl; 3 - hexogen; 4 - powder.

At the end of the previous section it was already noted that in melting explosives the surface zone of the condensed phase is a melt, and its state, therefore, does not depend on the relative density of the powder (at high densities). Taylor [193] connects

with this fact the independence of the mass rate of combustion from the relative density, which was observed during the combustion of PETN with the different dimensions of particles at a pressure of 52 at (Fig. 176). The mass rate of combustion is approximately constant; however, at small and great densities there is observed certain increase of it, which is similar to that, which was established by G. V. Oranskaya for nitrocellulose and, probably, determined for the same reason. Let us add that with the small density of PETN and considerable density of an inert gas, it would be possible to expect, because of dilution, a certain decrease in the rate, which, obviously, is overcome by the intensification of convection heat transfer, which leads to an increase in the rate. For coarse-grained PETN at small density (at great density crystals are crushed during pressing), the rate is distinctly greater than that for fine-grained, apparently, for the same reason.

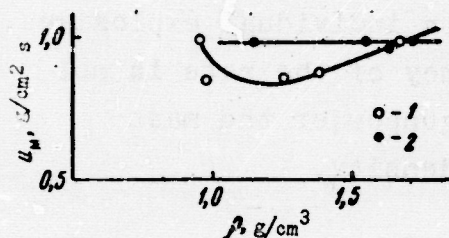


Fig. 176. Effect of the relative density on the mass rate of combustion of PETN at 52 at. 1 - dimension of the particles $\sim 5 \mu\text{m}$; 2 - 100-400 μm .

Somewhat less is the rate of combustion of powdery octogen with small density (Fig. 177), and the difference becomes more noticeable at high pressures when the dilution is greater. At 205 at this difference, apparently, decreases, possibly, because the penetration of gas products of combustion into the depth of the charge is affected.

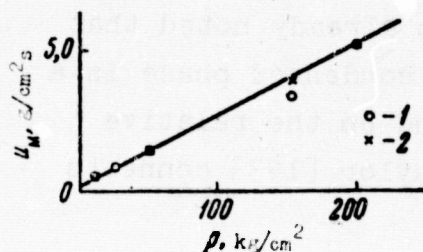


Fig. 177. Dependence of the rate of combustion of octogen of a different degree of dispersion upon pressure. 1 - dimension of the particles of crystals, 5 μm ; 2 - 124-152 μm .

Experiments of I. I. Polyakov with nitrocellulose (colloxylin), conducted in a wide interval of density (0.15-0.93), indicated that at a density of more than 0.6 the mass rate of combustion is considerably (approximately 1.5 times) increased with density. Yu. A. Rassulin, who worked with another specimen of colloxylin, which burned considerably more slowly¹ than that which was studied by I. I. Polyakov, did not detect at 1 and 3 at the effect of density on the rate of combustion, which remained constant. However, at 10 at and higher pressures, such a dependence was observed – the rate considerably increased with an increase in density (Fig. 1.78). It is true that in these conditions the effect of density can be partially connected with the dilution of explosives by an inert gas, which decreases with an increase in density. A similar effect of relative density on the rate of combustion was observed in the experiments of Yu. A. Rassulin during the combustion of PETN, the rate of which does not depend on density at 20 at and noticeably increases with density at 150 at; however, for tetryl an increase in the rate of combustion with an increase in density was observed neither at 20 nor at 100 at.

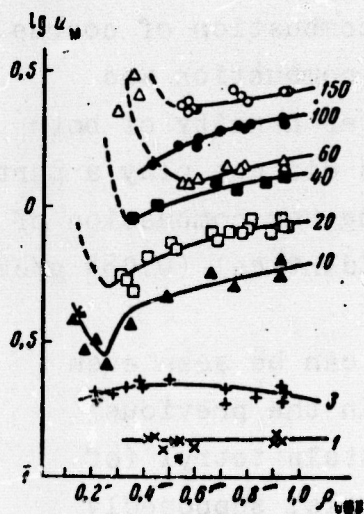


Fig. 1.78. Dependence of the rate of combustion of colloxylin upon density at various pressures (numbers near the curves). The dashed line denotes the region of a pulsating combustion

¹Different specimens of nitrocellulose with an identical content of nitrogen often were considerably different in the rate of combustion at atmospheric pressure; possibly, this is connected with the different content of mineral substances, which catalyze the combustion and which turned into nitrocellulose from a raw material (cellulose, acids, washing waters).

The effect of density on the rate of combustion can be associated with different reasons: with the change in thermal conductivity of the explosive, which can affect the rate of combustion (especially if in the condensed phase there is an exothermal reaction) and heat losses into the environment, and also the change in thermal effect on a unit of volume of the explosive, while the heat losses to the heating of the shell remain constant, and others.

For all the explosives studied at small densities the change in combustion on a pulsating accelerated mode was observed; the relative density at which this approached was greater with higher pressure (Fig. 178).

With great penetrability of the powder the rate of combustion can increase as a result of the penetration of gas products of combustion into the depth of the powder. In experiments with nitroglycerine powder pulverized into comparatively coarse powder the distinct effect of dimensions of the particles of powder on the rate of combustion was observed [81]. Fine powder with small density (0.4) burned at a reduced rate ($0.071 \text{ g/cm}^2\text{s}$), obviously, because the effect of the penetration of the gases into the narrow pores was practically not apparent. With the combustion of coarse powder this effect took place, and the rate of combustion was noticeably more ($0.092 \text{ g/cm}^2\text{s}$). With the greater density of both fractions (about 0.69) the penetration of gases did not play a part either during the combustion of coarse or during the combustion of fine powder, and the rates of combustion were identical ($0.084 \text{ g/cm}^2\text{s}$).

The effect of the penetrability of powder can be seen even during the combustion of melting explosives. In the previous section it was already noted that in large crystals tetryl (of small density) burned faster than in fine crystals, supposedly because of the penetration of fusion into the depth of the powder. Similar observations were made by Taylor during the combustion of

PETN and octogen at moderately increased constant pressures (Tables 27 and 28).

Table 27. Effect of the dimension of the particles on the rate of combustion of PETN at 27.2 at.

Diameter of particles, μm	Density of charge, g/cm^3	Mass rate of combustion, $\text{g/cm}^2\cdot\text{s}$
5	0,87	0,461
		0,480
353-500	0,96	0,516
		0,535
500-853	0,92	0,544
		0,531

Table 28. Effect of the dimension of particles on the rate of combustion of octogen at 12.6 at.

Diameter of particles, μm	Density of charge, g/cm^3	Mass rate of combustion, $\text{g/cm}^2\cdot\text{s}$
~ 5	1,02	0,48
67-76	1,05	0,52
104-124	1,04	0,56
200-600	1,19	0,69

The examined examples illustrate the simplest case when exothermal reactions occur predominantly in the gas phase, and when the role of density is limited by its effect on the penetrability of the substance for the fusion or gases and also on the thermal conductivity of the powder.

In general the dependence of the rate of combustion upon relative density can be more complex. Thus, for instance, in experiments of M. A. Rabinovich, for the mixture of barium saltpeter with iditol (89:11) with an increase in density in the region of small density a slight decrease in the rate of combustion is observed; with a further increase in density the rate of combustion rapidly increases; at great densities a sharp drop in rate is observed.

The unusual effect of density on the rate of combustion was observed in a number of ammonites [194], predominantly preventive (Fig. 179). With an increase in density from 1 to 1.7 g/cm^3 the

¹ Taylor explains the high rate of combustion of coarse-grained powder by the formation in this case of a certain microrelief of the surface of the liquid layer.

mass rate of combustion (under the pressure of nitrogen of 100-110 at) substantially decreases, although more rapidly, taking account the decrease in the dilution of the powder by an inert gas with an increase in density, and its reverse effect was to be expected.

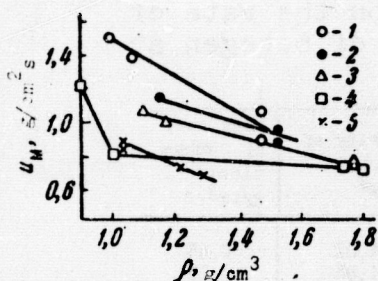


Fig. 179. Dependence of the rate of combustion of some preventive explosives upon cubic density at 100-110 at. 1 - Pobedit VP-3; 2 - Pobedit VP-1; 3 - waterproof ammonite PZhV-20; 4 - an ammonite No. 8; 5 - Pobedit PU-2.

3. Dependence of Critical Density of Explosives Upon Pressure

We saw that the disturbance of the uniformity of combustion and its transition into a pulsating mode with an increased rate is observed at atmospheric pressure when the relative density is decreased, in other words, the dimensions of pores in the powder up to a certain limit is increased. It is natural to expect that at a given relative density it is possible to obtain the transition in combustion from the normal into an accelerated mode if we increase the pressure under which combustion occurs. This conclusion was verified by experiments in the combustion of a number of powdery explosives at various constant pressures and at increasing pressure.

Combustion at constant pressure

Experiments were produced in various instruments of constant pressure. Data for the pyroxylin No. 1 are given in Fig. 180. At some definite density of the powder the mass rate of combustion at low pressures linearly increases with an increase in pressure.

However, this dependence is fulfilled only up to some pressure higher than which the rate of combustion starts to increase more rapidly and becomes of less uniform, although the disturbances of the uniformity of combustion still cannot be visually detected. With further increase in pressure the nature of the combustion is changed, and combustion becomes distinctly nonuniform and pulsating. The rate of combustion (more accurately the quantity of the substance which burns in 1 s on 1 cm² of the section of the charge) sharply increases and becomes even more fluctuating.

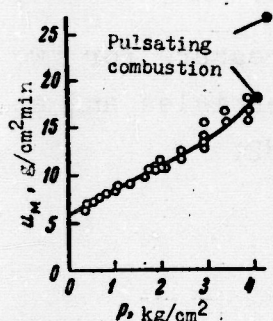


Fig. 180. Dependence of the rate of combustion of pyroxylin No. 1 upon pressure ($p = 0.37-0.45$ g/cm³, $d = 10$ mm, $t = 8-10^\circ\text{C}$).

The magnitude of critical pressure depends on the relative density, increasing with its increase (Fig. 181). The fact that the basic reason for the dependence of critical pressure upon density was in conditions of these experiments the effect of the latter on the penetration of the gases is indicated by the curve of Fig. 181, which depicts the dependence of the specific resistance of pyroxylin to the passage of air at small pressure drops upon cubic density [$r = \Delta p/v$, where Δp — pressure drop, mm H₂O per 1 cm of the length of the tube with a section of 1 cm², and v — volume of the passing air (in cm³/min)].

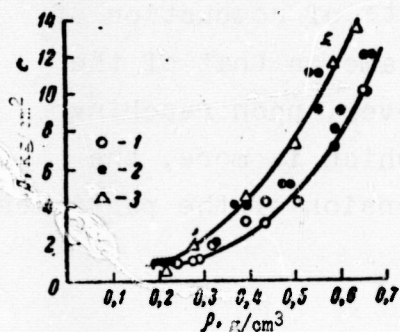


Fig. 181. Dependence of maximum pressure for pyroxylin No. 1 upon cubic density. 1 — uniform combustion; 2 — combustion with passage; 3 — specific resistance.

In a wider interval of pressures (up to 1000 at) the transition of combustion into an accelerated mode and characteristics of the combustion in this mode were studied by Chuyko [195] in the example of PETN, hexogen, and tetryl, and by Taylor - in the example of octogen, PETN and hexogen at pressures of up to 200 at. In experiments of Chuyko the explosive in the form of fractions with a definite dimension of the particles was pressed in portions into small plexiglass tubes with a diameter of 5 mm (thickness of the walls, 1 mm, and height 35 mm). Combustion was carried out in a bomb of constant pressure filled with nitrogen and was photographed on a rotating cylinder.

The dependence of the rate of combustion upon pressure for two specimens of PETN with different dimensions of the particles and at various relative densities are represented in Fig. 182.

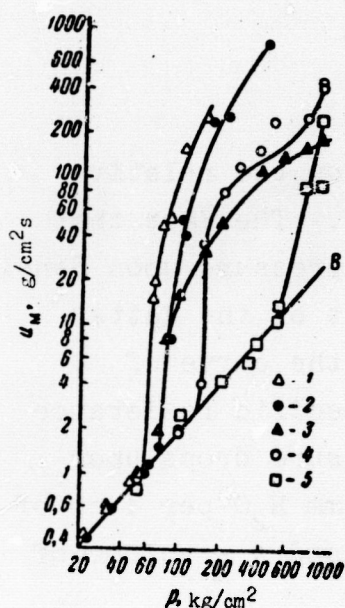


Fig. 182. Dependence of the rate of combustion of PETN (different dimensions of particles and relative density) upon pressure. B - dependence for a highly dense substance. Dimensions of particles (in μm) and densities (in g/cm^3): 1 - 200 and 0.57; 2 - 200 and 0.66; 3 - 5 and 0.28; 4 - 5 and 0.40; 5 - 5 and 0.66.

In the region of low pressures the mass rate of combustion of the powdery explosive of small density is the same as that of the pressed and also increases with pressure. However, upon reaching a certain critical pressure, the magnitude of which is more, the more the relative density and the less the dimension of the particles,

combustion passes over to an accelerated mode, and $\Delta u_m/\Delta p$ becomes much (10-120 times) more. The nature of the curve $u(p)$ is distinguished depending on density and, possibly, upon pressure, inasmuch as at various densities the change in the modes of combustion occurs at different pressures.

The dependence of the rate of combustion upon pressure in an accelerated mode is affected by two partially interdependent factors - the penetration of gas products of combustion into the depth of the powder, which actually is the reason for the increased rate of combustion, and dilution of the explosive by an inert gas is greater, the less the density of the powder and the more pressure. The penetration of gas products leads to the fact that combustion occurs not only on the end of the charge, but also in the layer of the powder of some depth and on the surface of its particles. According to the greater effective surface of combustion, in an accelerated mode the specific (per unit of surface of cross section of the charge) rate of a gasification is more. The fact that particles burn in the layer of considerable depth is indicated also in the observed, especially with coarse-grained powder, ejection of unburned substance deposited after the experiment on the bottom of the bomb. The dispersion of the substance intensely developed during the combustion of powders of small density is one of the stabilizing factors which determine the possibility of combustion with high rates without its transition into an explosion. The carrying away of the substance impedes the swelling of the layer of the burning suspended matter and limits the increase in pressure connected with it in the zone of combustion.

The dilution of powder of explosives of small density lowers the temperature of the gas products which penetrate the powder being contained in the latter by an inert gas. The effect of the dilution is especially clearly indicated in Fig. 183, which shows the change in the rate of the combustion of firely crystalline PETN depending on density. The drop in the mass rate of combustion

with an increase in density (branch *BC* of the curve) is entirely natural and is the consequence of the decrease in clearances between the particles, and, consequently, the gas permeability of the powder. The ascending branch of the curve *AB* can, obviously, be explained only by the decrease in the dilution, which appears especially greatly at high pressure (density) of an inert gas and small relative density when the portion of the volume falling on the pores is great. At a density of 0.27 and 1000 at the nitrogen content in powdery PETN is 44.5% and at a density of 0.4, ~28%.

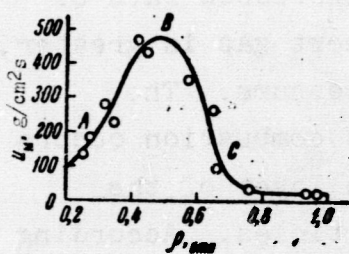


Fig. 183. Dependence of the rate of combustion at 1000 at of finely crystalline ($d = \mu\text{m}$) PETN relative density.

In conditions of experiments at constant pressure dilution has a unique stabilizing effect on the stability and especially the nature of the accelerated combustion. The higher the pressure, the greater the rate of combustion and dynamic increase in pressure in the front, which forces the gases of combustion to penetrate the depth of the powder, and the higher the effective temperature of the latter. However, simultaneously the increase in pressure, intensifying the dilution, lowers the temperature of the gases, increases the heatcapacity of the mixture explosive + inert gas, and reduces the temperature of combustion, i.e., its rate.

In the region of moderately increased pressures (75-450 at) for finely crystalline PETN with an increase in density, which leads to an increase in the pressure of separation, the dilution remains approximately identical; and the ratio $\Delta p_{\text{max}}/\eta$ greatly decreases. This indicates the fact that a predominant effect is seen in the increase in temperature of the gases (as a result of the increase in completeness of conversion) penetrating into the powder.

At high pressures (1000 at) the role of this factor, naturally, decreases, and dilution obtains a predominant importance.

On the whole dilution, to a greater or lesser extent, balances out the effect of the penetration of gases. In this case in those conditions where the gas permeability is great (small density), or the gas-dynamic increase in pressure is great (high pressures, i.e., the high rates of combustion), dilution is also great. Therefore, favorable conditions for the penetration of combustion can be realized only when this penetration occurs at relatively low pressures, i.e., either in coarse-grained powder or for an explosive with a high rate of combustion. Actually, the greatest increase in the rate of combustion was observed in coarse-grained PETN and hexogen at comparatively moderately increased pressures. Attention is given to the fact that the continuously accelerated combustion of finely crystalline PETN was observed at a certain average density and pressure; at high density penetration was started at high pressure when dilution was already great; at small density it started early, but at this pressure the rate of combustion and the dynamic increase in pressure were still small. At average pressures all conditions can be combined, which favorable to the development of penetration — a sufficiently high rate and temperature of the gases of combustion and not too great a dilution of the explosive.

The fact that with a moderately condensed fulminating mercury the penetration of gases of combustion is so great is natural, which leads to the transition of combustion into detonation at atmospheric pressure. One of the reasons for this is the high rate of combustion of fulminating mercury. During the combustion of secondary explosives, which possess at atmospheric pressure considerably smaller rates and effective temperatures of combustion, the dynamic increase in pressure is insufficient to provide the intense penetration of combustion.

The photographic recording of the combustion of explosives in an accelerated mode shows some of its characteristics. In comparison with a normal combustion, its front is washed away, especially during the combustion of coarse-crystalline powder; movement of the front is less even - sometimes this nonuniformity has the nature of passages, and sometimes it is of a smaller scale and has a relatively "uniform" nature. Light emission usually has a nonuniform banded structure. A frequent type of it is that which was observed during the combustion of tetryl (Fig. 184). An accelerated mode possesses known stability and usually, having appeared once, no longer passes over into the normal mode; the average magnitude of the rate is approximately constant - in individual experiments, however, its continuous increase was observed. The characteristic of the accelerated mode is also the nature of light emission at the end of combustion: it is continued (unlike normal combustion) more or less for a long time.



Fig. 184. Photographic recording of the combustion of tetryl in an accelerated mode.

With the nonuniform combustion of hexogen and especially tetryl, on photographs individual and almost horizontal intensely glowing steps are apparent. Their formation, apparently, is connected with the penetration of hot gases into the depth of the powder by individual streams. The flowing penetration of gases in the mode of the accelerated combustion is indicated also by experiments, in which the bottom of the charge is a thin paper. The traces of the action of high temperature were on it in the form of individual spots, while during normal combustion the firing was uniform.

Conditions and results of experiments of Taylor are similar to those described above. The effect of the dimensions of particles of octogen on the transition of combustion into an accelerated mode is shown in Fig. 185. The fine (5 μm) powder even at small density in the whole studied interval of the pressures burned in the normal mode at a rate linearly growing with pressure; more coarse-grained specimens gave the transition into the accelerated mode, which approached earlier, the coarser the particles were. The dependence of the rate of combustion upon pressure during combustion in a rapid mode is greater for coarse-grained powder, and in experiments of Taylor PETN and hexogen burned similarly.

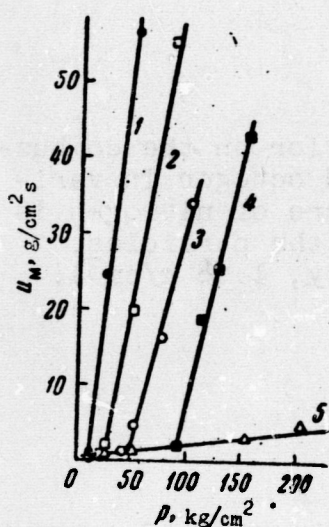


Fig. 185. Rates of combustion of pressed powder of octogen at various pressures. Dimension of particles (in μm) and density (in g/cm^3): 1 - 200-600 μm and $\rho = 1.20$ g/cm^3 ; 2 - 104-124 and 1.05; 3 - 64-76 and 1.07; 4 - 53-64 and 1.08; 5 - 5 and 1.02.

For confirmation of the mechanism of combustion in a rapid mode Taylor conducted experiments on combustion in plexiglass tubes with a length of about 8 cm in three variants: 1 - with an enclosed lower end; 2 - with the lower end enclosed grid; 3 - with the lower end enclosed by a grid and narrowed approximately two times by an upper opening. Results of experiments which were produced with coarse-grained octogen (200-600 μm) are presented in Fig. 186. The initial rate of combustion in all three variants is identical. Subsequently, however, combustion is accelerated - most of all in

the third variant and less in the second. With a decrease in height of the remaining column of explosive, its resistance decreases, and correspondingly the penetration of gases from the front is intensified. In the first variant, on the contrary, on the last centimeters combustion is retarded, obviously, on account of the fact that the penetration of gases is impeded by appearing counterpressure, which does not appear with the second variant. In the third variant the contraction of the output section of the tube creates an additional increase in pressure, which is added to its dynamic elevation, in consequence of which the penetration of gases into powder is intensified. Increase in pressure by itself is too small in order to explain the observed increase in the rate of combustion.

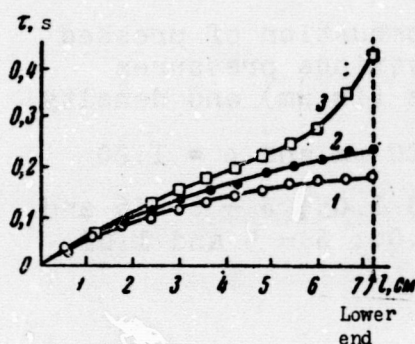


Fig. 186. Data of Taylor on the combustion of coarse-grained octogen in various conditions (pressure of nitrogen is 27.2 at, dimension of the particles, 200-600 μm , and density, 1.08 g/cm^3).

Kondrikov [196] studied the dependence of the rate of combustion of some powders (in the form of a shaving) upon the relative density (Fig. 187). In the region of small densities the rate rapidly increases with density, passes through the maximum at which the linear rate by 30-70 and more times exceeds the normal rate of combustion, and then it drops, approaching the rate characteristic for a solid substance. With a further increase in density up to its maximum value, the rate of combustion increases slightly. The maximum of the rate is reached for different powders at various values of the relative density, which do not show the direct dependence on the magnitude of the normal rate. The values of the ratio u_{max}/u_n are also greatly different.

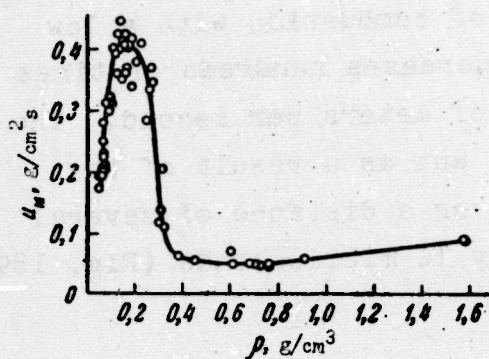


Fig. 187. Dependence of the mass rate of combustion of the powder N shaving upon the density comparative of the charge.

Combustion in a rapid mode occurs unevenly, and its rate first sharply increases and then drops; a considerable part of the burning particles is taken away by gases from the surface of the charge and burns far from it. It is possible to detect by direct observation that the gas products of conversion with particles of smoke suspended in them are propagated, leading the flame by a centimeter and more. The reaction zone becomes wide, and in contrast to normal combustion, apparently, the wider it is, the higher the rate of combustion. One of the characteristics of the rapid mode of combustion is the great dependence of its rate upon the diameter; thus, with an increase in the latter of 5 times, the rate increases by more than 5 times. It increases greatly also with pressure (Fig. 188).

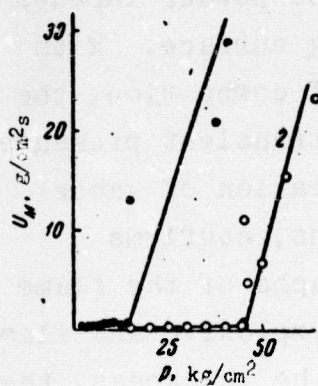


Fig. 188. Effect of pressure on the rate of combustion of gunpowder shaving. 1 - mixture powder; 2 - Powder N.

The mode of rapid quasi-stationary combustion is retained on the condition that the length of the tube is not too great. Otherwise, after a considerable section of combustion with a low and almost constant rate, it suddenly increases hundreds of times and reaches values of the order of hundreds of meters per second. The high rate was reached not spasmodically, but as a result of the progressing acceleration of combustion over a distance of several tens of centimeters and for approximately 10 milliseconds (Fig. 189).

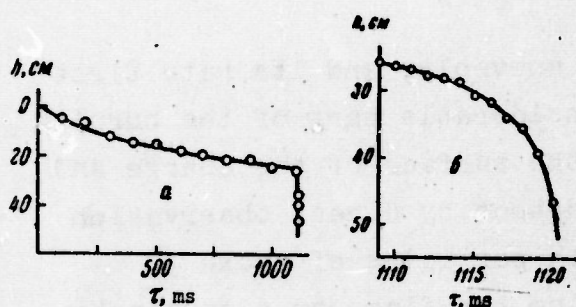


Fig. 189. Combustion of gunpowder shaving in a charge of small density placed into a long glass tube. Photographing by camera SKS-2M with a frequency of 1000 frames/s (h - distance from the upper end of the charge, τ - time; a) whole charge; b) part of the charge in which explosion occurred).

In the transition of combustion into an accelerated mode the sharpness of this transition draws attention, although if we consider, that it is conditioned by only the dynamic increase in pressure, it would follow to expect a rather gradual increase in the rate of combustion according to a gradual increase in dynamic pressure. Taylor (independently of Belyayev) expressed the assumption that the penetration of combustion into the depth of the powder impedes the layer of fusion which is formed on the burning surface. With an increase in pressure and, consequently, rate of combustion, the thickness of the molten layer decreases and with transient pressure it becomes too fine in order to prevent the penetration of gases into the powder. Besides using logical conclusions, confirms Taylor the reality of the molten layer by photographs of the flame (Fig. 190), visible on which the boundary of the explosive and flame is a narrow strip of greater width, and the less the thickness, the greater the pressure and rate of combustion. He explains, the

smaller width of the image of the flame by the deflection in the rays because of the different density of the products of combustion and glass; the small width of the image of the column of powder is explained by the fact that because of the poor optical contact of particles with the glass on the periphery of the charge there occurs a deflection in the rays, which do not enter therefore, into the objective.



Fig. 190. Front of the flame of PETN with a glowing line, which corresponds to a molten layer. A - glowing line visible along the whole diameter of the slot, B - limit of visibility of the powder.

The dependence of the critical pressure upon the dimension of the pores and the great ease of the transition of combustion into an accelerated mode for high-melting (278°C) faster burning octogen in comparison with PETN¹ melting considerably lower (140°C) is considered by Taylor as confirmation of the role of the molten layer noted above.

¹Taylor does not take account that the boiling point of PETN (270°C) is much lower than the unknown [but in any case greater than that of hexogen (340°C)] boiling point of octogen. Therefore, the question about the fact that for which explosive the layer of the fusion will be thinner, cannot be evaluated only according to the melting point and rate of combustion.

A known difficulty for the Taylor's treatment is the fact that for nitrocellulose, as we have seen above, regularities similar to melting explosives are observed. He bypasses this difficulty by considering that during the combustion of nitrocellulose the molten layer, which impedes with its great thickness the penetration of combustion into the depth of the powder is also formed.

Although the presence of a molten layer during the combustion of low-molecular explosives is indisputable and was repeatedly noted and used earlier for the explanation of some phenomena taking place during the combustion of melting explosives [197], specifically, as an obstacle for the penetration of gases of combustion into the depth of the porous powder, the observations made during the study of the transition of the combustion of powders on an accelerated mode can be explained differently than the way Taylor did it.

The factor directly causing the penetration of gases into the depth of the powder is the dynamic increase in pressure, which appears in the burning surface as a result of the outflow of gases. This increase in pressure, as we will see below, is proportional (at small values of it) to the rate of combustion, i.e., it rapidly increases with an increase in pressure over the burning charge. Since, furthermore, at increased pressures the density of gases will be more, then their mass and internal energy penetrating into the depth of the powder will increase even more rapidly. Therefore, by increasing the pressure (during combustion under constant pressure), it is possible to obtain the effect of the advance by gases of the front of combustion not only at small but also increased densities of the powdery explosive. In this case, the higher the density, the greater should be, other conditions being equal (specifically, equal dimensions of the particles), the pressure, beginning from which the indicated effect appears. At exactly equal density the possibility of the penetration of gases should depend on the dimension of the particles, which determines the dimensions of the pores, in other words, the resistance of powder to the penetration of the gases. One should expect also that, other conditions being

equal, the explosive with greater rate of combustion will at greater density or at lower pressure give a disturbance to the normal rate of combustion.

The effect of the rate of combustion is clearly evident from results of experiments given by A. F. Belyayev on the combustion of fulminating mercury at atmospheric pressure and various relative densities (Fig. 191). The noticeable increase in the rate with a decrease in density is observed at a density of about 0.68, and at a density of 0.64 it sharply increases and sometimes even detonation approaches.

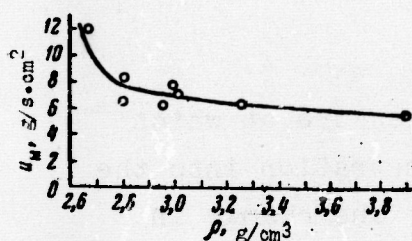


Fig. 191. Dependence of the rate of combustion of fulminating mercury upon cubic density.

Thus, the effect of the penetration of gases into the depth of the powder during combustion by a rapidly burning fulminating mercury is seen at atmospheric pressure with a decrease in density down to 0.7 of the specific weight,¹ while the relatively slowly burning nitrocellulose this is observed only at a density of about 0.12 of the specific weight. For nitrocellulose with a relative density of 0.7, the critical pressure is 40-50 at.

¹It would be more correct to make a comparison not with respect to the volume of the pores but with respect to their cross section. However, the magnitude of this section depends on the magnitude of the particles and also their form with respect to which there are no data. Furthermore, the decrease in dimensions of the particles increases their surface; ultimately, although the penetration of gases is impeded, the intensity of the combustion formed increases. In general, it is difficult to evaluate the total effect of all these factors.

If the penetration of combustion into the depth of the charge was determined only by the magnitude of the dynamic increase in pressure, then one should expect the constancy of the ratio $\frac{\Delta p_{\text{dyn}}}{r}$ (where r — the specific resistance of the powder to the penetration of the gases). Moreover, at the given dimension of the particles, inasmuch as an increase in resistance by means of an increase in density of the charge is accompanied by an increase in the quantity of the substance in a unit of a volume, it was to be expected that the ratio shown will increase with increased pressures of the disruption of normal combustion, which are characteristic for greatly condensed powders. In actuality, the higher the pressure of the disruption, the less the corresponding value $\Delta p_{\text{dyn}}/r$. This decrease appears especially sharply in the region of moderately increased pressures — up to 100 at.

Hence it follows that the effect of the pressure at which combustion occurs on the possibility of its penetration into the depth of the powdery charge is not exhausted by the change in dynamic increase in pressure.

It is known that the combustion of explosive occurs, as a rule, in steps, and at low pressures it cannot reach the end and stops at a certain intermediate stage. In this case the liberation of heat is incomplete, and the temperature of the gas products of combustion is relatively low. At the same time it is clear that the igniting ability of the gas products of combustion, naturally depend on their temperature. The passage of the stopped conversion of explosives during combustion to a great degree depends on the pressure; the increase in pressure facilitates its passage. For different explosives the limit of pressure, starting from which the conversion in definite conditions of combustion reaches the end, is different. Therefore, the real temperature, attainable during combustion at a definite pressure, depends on the magnitude of the latter.

This finite temperature is reached not directly at the surface of the explosives, but at the same distance from it, and the less it is, the higher the pressure. Therefore, even at pressures lying above that at which the completeness of the conversion is reached, the temperature profile near the surface of the explosives is different: at low pressures the mean temperature of the layer of definite thickness is less than that at high pressures. Since, as was already mentioned, with the increase in pressure and density of gases increases, then the increase in the internal energy of the layer of gases adjacent to the burning surface becomes even more per unit of their volume.

According to these three reasons, the igniting action of gas products of combustion with an increase in pressure can greatly increase.

It is obvious that for those explosives whose temperature of combustion is higher at the given pressure, the zone with the maximum temperature is located nearer to the burning surface, and the penetration of the combustion into the depth of the charge and its transition from the normal into the accelerated mode will occur easier with less gas permeability of the charge. In turn, at the given porosity of the powder the pressure, starting from which the mode of the penetration will be carried out, for such explosives will be less.

However, the penetration of gas products of combustion into the pores of the powdery charge is still not identical to the penetration into them of the combustion itself. It is insufficient to ignite explosives on the internal surface of the pores, and it is necessary that combustion could be developed in them. This depends, besides the nature of the explosives, upon the diameter of the pores and upon their length¹ and pressure. It is known that

¹The closed pores, not connected with each other, for example, in the form of bubbles, can lead only to a certain increase in the mean rate of combustions without the disturbance of its uniformity. On the contrary, deeply penetrating pores, as they exist in usual pressed powder, under corresponding conditions can lead to the disturbance of the uniformity of combustion.

with ignition on the end of the charge of an infusible powdery explosive the combustion occurs only when the density and, respectively, thermal conductivity of powder, which determines the heat removal from the surface, are not too great.

Similarly, in a channel (pore) of a small diameter the heat removal in a radial direction can be so great that it will not be completely compensated by an increase in heat.

However, besides this physico-geometrical aspect, there is also another important aspect of the phenomenon. It is known that the initial reactions of the conversion of explosives, as a rule, liberate comparatively little heat and sometimes are even endothermic. Secondary reactions occur when an explosive burns along the free surface at some distance from it. If close to this surface there is a cooling body, for example, the surface of a plate of metal which conducts heat well, then secondary reactions are not carried out. A similar phenomenon takes place in the close arrangement of gunpowder surfaces, for example, in a channel small diameter of a gunpowder tube. With the increase in diameter of the channel combustion becomes possible.

An increase in the length of the channel impedes combustion for the reason that the rate of the gas flow along the burning surface increases. This, on the one hand, can lead to an increase in the rate of combustion in the channel and to an increase in pressure in it, which leads to the burning of the heated layer; the subsequent drop in pressure can lead to extinguishment. On the other hand, the high rate of motion of gas products of combustion in a narrow channel can lead to the mixing of cold internal layers and inhibit the completion of reactions in the latter.¹

¹This phenomenon is similar to that which is observed with the approach of agitation of the combustion of nitroglycerine at low pressures, which leads to the extinguishment of combustion.

For these reasons combustion in narrow pores at low pressures is unstable. If combustion penetrated into a pore of small diameter, then it will be ejected from it. This ejection can be so energetic that combustion is extinguished. The increase in pressure accelerates the gas-phase reactions during combustion, and when the thickness of the zone of conversion decreases down to dimensions of the order of the radius of the pore, combustion in the pores becomes possible. Then for the penetration of combustion into the pores, even that small dynamic increase in pressure, which appears during normal combustion becomes sufficient.

The penetration of combustion into the pores according to the increase in the actual surface of combustion greatly increases the dynamic increase in pressure, i.e., the driving force of the penetration of gases. Then this penetration should be developed unlimitedly, providing there are no factors counteracting this development.

Thus, the dynamic increase in pressure of normal combustion for the conditions mentioned above will only be provided by a special mechanism which will force combustion to penetrate the pores; after this the penetrating combustion will become a process which is generated independently.¹

Some of the factors which impede the acceleration of convective combustion can be the combustion of particles on the surface of the charge, which moves this surface in the direction of combustion into the depth of the powder. It can help remove the particles carried along by swift gases, owing to which the effective depth of the layer of the burning suspended matter remains constant.

¹In experiments on combustion under increasing pressure, the pressure necessary for the transition into a rapid mode is many times more than dynamic increase in pressure. This also indicates the fact that for increased pressure normal combustion serves only as the initial impulse in the formation of the mode of rapid combustion.

However, the constancy by itself of the thickness of the layer of the burning suspended matter of particles of explosives is still not a sufficient condition of the stationary state of the process. It is important also that this thickness (more accurately the magnitude of gasification) does not exceed the determined boundary, which at a given pressure corresponds to the quantity of gases flowing away. If the gasification is greater than the gas removal and increases with pressure not in proportion to it but more rapidly, then the equilibrium pressure during combustion does not exist - it increases and correspondingly convective combustion is accelerated.

Where prerequisites for the acceleration of combustion are absent, convective combustion is extended in a quasi-stationary manner at rates at tens and hundreds of centimeters per second, as this was observed in experiments by Chuyko, Taylor and Kondrikov.

If limitations for the acceleration of combustion are absent, then there appear processes which are propagated at rates of several hundreds of meters per second, which easily lead to the formation of shock waves and detonation.

The role of the removal of the particles in the development of a convective combustion was illustrated by B. N. Kondrikov by the following experiment. Under definite conditions the charge, consisting of coarse-grained powder, burns rapidly but stably with a constant rate; if the powder is slightly moistened with acetone so that its grain, without changing its dimension, were stuck from together and then the acetone is removed, then the combustion of such a charge rapidly is accelerated, since the removal of the particles becomes impossible and the thickness of burning layer continuously increases.

Convective combustion differs by certain characteristics. The sensitivity of its rate to external pressure is much more than that of normal combustion. The rate of the latter is determined by the total pressure (external pressure + relatively a low dynamic

increase in pressure). The rate of convective combustion is determined, first of all, by the rate of the penetration of gases dependent on the dynamic increase in pressure. The relatively small change in external pressure will be great with respect to the dynamic increase in pressure, and it can greatly affect the rate of convective combustion.

This effect is so great that the combustion passes over from a stable convective mode to an accelerated one even if the large length of the charge in the tube is taken. With the deepening of combustion from the upper section of the tube the resistance of its freed section to the discharge of the gases more and more stops, and, finally, the increase in pressure induced by this proves to be sufficient to provide the thickening of the burning layer and, correspondingly, the acceleration of combustion. Natural also is the inconstancy of the rate in transient region. When the external pressure is increased to such a value at which for the given explosive the penetration of gases can occur, then it occurs in the beginning only in a few largest pores, the number of which is small and inconstant. Only with a further increase in pressure all or a large part of the pores start to "work" and the effect of the large pores on it dwindles down to nothing.

The rate of convective combustion is greatly affected, as B. N. Kondrikov indicated, by the diameter of the charge, and this effect is not determined by its usual effect on the relationship of heat losses and increase in heat. One of the possible explanations of this effect consists in the fact that with a large diameter on the total surface of the charge there are larger pores, according to which combustion is propagated easier.

One should show that if combustion penetrated into the pore, then further process is selfdeveloping, since the flare-up of the pore makes combustion in it, as a rule, more stable.¹

¹This fact, possibly, play a role during the development of burn-out in gunpowder charges.

A definite role is played by the depth of the pore. If it is too great, then the rate of combustion of walls of the pore can be strengthened due to the high rate of the gas flow along it. This in turn leads to pulsating combustion and in the limit and to pulsating effect. On the other hand, the propagation of combustion in the pore only with its small depth is determined by external pressure. If depth is great and the resistance to the output of the gases became considerable, then the leading role can pass from external pressure to internal, and combustion starts to be accelerated independently of external pressure.

This explains that paradoxical fact that at the given magnitude of the powdery charge under definite conditions of combustion the increase in height of the charge (with a corresponding decrease in diameter) leads to an increase in the intensity of combustion, although conditions for the penetration of gases into the powder (at the given external pressure) are impeded.

Combustion with increasing pressure

In the previous section we examined the transition of normal combustion into an accelerated mode as a result of the penetration in the porous charge of gas products of the combustion, which is started under the effect of that local increase in pressure which appears near the burning surface of the charge.

Much more favorable conditions for the penetration of combustion into the depth of the porous charge are carried out if it occurs under increasing pressure, as, specifically, takes place in a firing weapon of the barrel type. In this case the penetration of gases into pores occurs not only because of the local increase in pressure of the front of combustion, but also as a result of the pressure rise in the whole volume of the gases. Therefore, even small penetrating porosity leads to the disturbance of normal combustion. Namely, this fact was in its time one of the basic motives of the

failure of black powder and the change to colloidal type of powder. Even at considerable technologically real densities, Vieille observed at high increasing pressures the disturbance of the normal combustion of black powder, which did not make it possible to regulate in the proper measure the duration of the combustion. He showed also that such a control is possible if black powder is pressed under very high pressures, which gives a density close to the specific weight.

Smokeless powders, because of the cohesion and strength of their particles, provide the normal mode of combustion in the whole range of pressures interesting to technology.

Investigations on the combustion of explosives under increasing pressure were produced basically by two methods: in so-called Andreyev tubes and in the Vieille manometric bomb.

The first method consists in ignition on the end of a considerable (50 grams and more) charge of explosives in a steel vessel; the vessel has a cover with an opening of large cross section, closed by a metal disc, which breaks loose upon the reaching of a definite pressure. With little strength of the disc combustion leads to its breaking loose without the breakdown of the completeness of the vessel. At great strength, despite the extraction of the disc the vessel is broken into a larger or smaller number of pieces (Fig. 192), which in the limit corresponds to that, which provides detonation induced by the percussion-cap detonator. The minimum strength of the disc, beginning with which the failure of the vessel occurs, serves as a measure of the tendency of the combustion of the explosives toward the transition into an explosive mode..

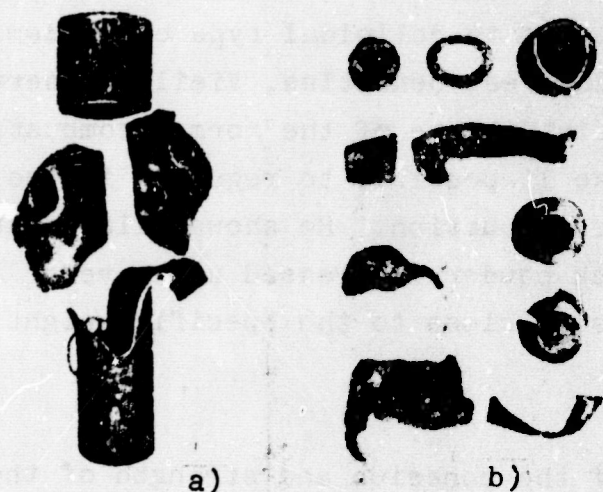
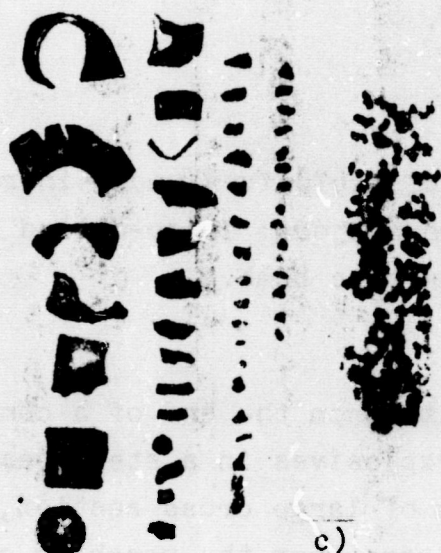


Fig. 192. Three types of the rupture of a tube: a) with combustion; b) with explosion; c) with detonation.



Usually a vessel (Fig. 193) with a diameter of 40 mm, a thickness of the wall of 4-6 mm and a height of 200 mm was used. The diameter of the opening of the cover was 30 mm; it is closed by a disc of lead (or other metal), the strength of which is determined by experiments on the combustion in a vessel of coarse-grained smokeless powder. Such calibrating, naturally, determines the strength of the disc in reference to the relatively slowly growing pressure; with a rapid increase in pressure accelerative resistance of the disc acquires importance also. The limit of strength is the resistance to the rupture of the glass itself, which at the indicated dimensions constitutes about 1000 at. Ignition is produced usually

with the help of a two-gram charge of a pyrotechnic composition (KNO_3 -68%, Mg-20%, iditol - 12%), ignited with the help of a quick match and incandesced by the current of a wire. For an increase in the density of the charging, the vessel can be filled with gypsum at a certain height.

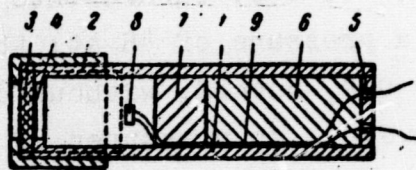


Fig. 193. Tube for experiments on combustion under increasing pressure: 1 - iron housing; 2 - iron cover; 3 - lead plate; 4 - asbestos plate; 5 - iron bottom; 6 - gypsum; 7 - explosive; 8 - ignition charge; 9 - lead for ignition.

In one of the variants of the method caps for the vessel with a small open eyepiece of a definite cross section are used. The diameter of the eyepiece, which demarcates the absence and presence of the rupture of the vessel, is taken as the measure of the tendency of combustion of the tested explosive toward the transition into an explosion. This variant is less reliable than the one described above, since the possibility of the outflow of gases through the eyepiece impedes ignition of the explosive and can even lead to the extinguishment of the initiated combustion as a result of the rapid drop in pressure. Therefore, the negative result of the experiment can be the consequence of not the stability of combustion of the explosive, but of its poor combustibility; the metal disc provides reliable ignition. The application as an igniter of pyrotechnic composition, which develops high temperature at relatively low pressure not able to force out a disc of standard strength, also provided the reliability of ignition.

Experiments indicated that for each explosive there is a certain limit of strength of the disc above which the ignition provides the transition of combustion into an explosion, which is accompanied by

the rupture of the vessel. However, the magnitude of this limit depends not only upon the nature of the explosive. The same explosive behaves completely differently depending on the relative density, i.e., upon the degree of porosity.

Thus, in one of the works the combustion of powdery hexogen (relative density from 0.4 to 0.6) turned into detonation (charge of 50 grams) already at a pressure of 45 at; the hexogen, pressed to a density of close to 0.9, burned, without detonating, even at a pressure of 700 at; however, at pressures of 200 at a certain fragmentation of the vessel, which indicates a combustion accelerated in comparison with the normal there was observed above.

The combustion of powdery PETN of small density (about 0.6) also turned into detonation with the acquisition of the disc, which breaks loose at 45 at; in this case the combustion of pressed PETN ($\rho \sim 0.96$) leads only to breakaway of the disc without the breakdown of the completeness of the vessel, and only at a pressure of 500-700 at in two of three experiments was there observed detonation. At a smaller density (0.92) the breaking of the vessel was observed already with the disc with standing a pressure of 210 at.

The nature of the combustion is affected also by the magnitude of the charge. Thus, with a disc, which breaks away at 40 at, a charge of PETN with a weight of 10 grams (dimensions of the particles, 0.25-0.5 mm) did not cause breaking of the vessel,¹ such a breaking was observed with an increase in the weight of the charge up to 13-20 grams. The effect of the magnitude of the charge is established for hexogen; however, other conditions being equal, the transition of combustion into an explosion occurred, starting from the magnitude of the charge of 22 grams, almost two times larger than that for PETN.

¹Under the charge of powdery PETN cast trotyl was placed. The absence of its explosion served as additional evidence of the fact the combustion of PETN did not turn into detonation.

The minimum magnitude of the charge providing the change in combustion into an explosion decreases with an increase in the strength of the disc. With a disc, which withstands a pressure of 260 and 400 at, a ten-gram charge of PETN provided the transition of combustion in an explosion, which was not observed with a disc with a strength of 40 at. The same effect of the strength of the disc on the minimum magnitude of the charge was observed for flegmatized hexogen, but, naturally in the region of great magnitudes of the charge.

Playing role also is the height of the charge, the increase of which within certain limits (at its constant magnitude) favors the transition of combustion into an explosion. Thus, the increase in height of the ten-gram charge of PETN from 9 mm, at which an explosion did not occur, to 14 mm led to the change in combustion in an explosion.

A considerable effect on the stability of combustion was rendered also by dimensions of the particles of the explosives. If the dimension of particles of PETN were 0.01 mm, then the transition of combustion into an explosion was observed, starting from the magnitude of the charge equal to 10 grams, at 0.25-0.5 mm - starting at 12 grams and at 1-2 mm - starting at 40 grams. Charges with a weight of 50 grams with the strength of the disc of 20 at were detonated if the dimension of the particles were 0.01 and 0.25-0.5 mm; if the dimensions of the particles were equal to 2-3 mm, only combustion was observed.

In the combustion of fine hexogen the transition of combustion into detonation was observed if the dimension of the particles was 0.1-0.25 mm, the weight of the charge 50 grams, the strength of the disc 22 at and the density 0.5-0.6; at 17 at combustion occurred without the breaking of the vessel. For charges of hexogen, which consisted of crystals with a dimension of 0.5 mm and 1-2 mm, at the

strength of the disc of 38 at the transition of combustion into an explosion was observed, but the fragmentation of the vessel was much less. With an increase in the dimension of the crystals up to 2-3 mm and more the strength of the disc necessary for an explosion is sharply increased, and the transition of combustion into an explosion is not observed even with the strength of the disc exceeding the strength of the vessel (1000 at).

It is natural to expect that the excessive decrease in dimensions of the particles will hamper the transition of combustion into an explosion because of the decrease in the gas permeability. For PETN and hexogen at the dimensions of particles used and relatively low density this effect was not revealed. However, was distinctly observed for the mixtures of ammonium perchlorate with aluminium powder; with the dimension of particles of perchlorate at 10 μm (the dimension of particles of aluminum at $\sim 1 \mu\text{m}$) and relative density of 0.56, transition of combustion into an explosion was not observed in the whole interval of the strength of the disc (22-1500 at); if the dimension of the particles was equal to 40 and 120-150 μm , an explosion occurred with the strength of the disc at 20-25 at; with the use of large particles (50-1000 and 1000-2000 μm) an explosion at this strength of the disc was not observed.

The flegmatization of PETN and hexogen with a mixture of stearin and ceresin considerably increases the pressure at which combustion turns into an explosion. If an inert admixture is added in the powdery form (starch), then its flegmatizing action in the relationship to the transition of combustion into an explosion is considerably weaker.

Exploding relatively easily (starting from the strength of the disc of 100 at) with ignition also are mixtures (82:18) of ammonium nitrate (predominant dimension of the particles, 0.1-0.25 mm) with aluminium powder (1 μm); an explosion is obtained even somewhat easier than it is for a trotyl mixture (82:18).

Mixtures of ammonium perchlorate with aluminium powder behave even more actively. Ammonium perchlorate itself is quite inert and did not provide an explosion in the whole range of the strength of the disc (50-1500 at). With the content in it of 5% powder the fragmentation of the vessel is observed at a strength of the disc of 22 at; the breaking of the vessel, although by a smaller number of pieces, was observed also with an addition to the perchlorate of 9 and 18% aluminum; at 28% aluminum (a stoichiometric mixture) an explosion was not observed even at 1000 at. A mixture of ammonium perchlorate with trotyl (84:16) behaves considerably more inertly, than does aluminum; it explodes at 400 at and an explosion does not occur at 260 at.

Other powdery explosives studied give a similar picture of the destructive action depending on relative density. However, the vessel breaks more slightly, than in experiments with PETN or hexogen. Ammonites on a base of tetryl (79:21; 88:12) with a filled density only at a pressure of less 200 at do not break the vessel; at a pressure of 500-700 at its considerable fragmentation, close in intensity to detonation is observed; at a pressure of 1200 at all the ammonites detonate.

Powdery tetryl ($\rho \sim 0.6$) only with the strength of the disc of 45 at does not produce fragmentation of the vessel; at a pressure of 65 at the vessel is broken into a small number (3 and 4) pieces; the increase in strength of the disc intensifies fragmentation, but even at a pressure of 500-700 at detonation does not occur both with a charge of 50 grams and a charge of 150 grams.

Picric acid ($\rho \sim 0.6$) at a pressure of 500-700 at causes even weaker fragmentation, the intensity of which somewhat increases with an increase in the weight of the charge. In the shell, which is broken at 1200 at and with a charge weighing 425 grams at the same density, picric acid provided detonation. Xylol and trinitrobenzoic acid indicate the similarity in behavior, which yields in intensity of the fragmentation of the vessel to picric acid.

The combustion of trotyl¹ causes slight breaking of the shell. Trotyl with strong disc, as a rule, burns and breaks the vessel, not crushing it. Even in shells which are broken at pressures of 1200 and 1600 at are wholly filled with crystalline powder ($\rho \sim 0.55$), and combustion does not turn into detonation, and only moderate fragmentation of the shell is observed. Granulated trinitronaphthalene is close to trotyl in an effect.

Dinitro compounds, naturally, are more inert in the described conditions of the experiment than even trotyl - their combustion frequently is extinguished, not leading to the breaking of the vessel.

In a pressed or cast form tetryl, picric acid, and ammonites even at the pressures of 500-700 at only burn. Experiments on explosives placed into more durable shells (the pressure of breaking, 1200 and 1600 at) indicated that under these conditions with the charge of the trotyl of 570 grams fragmentation of the shell is much weaker than that with detonation; cast picric acid in a shell, which is broken at a pressure of 1200 at produces its slight fragmentation.²

¹Apparently, in the case of the combustion of trotyl a substantial effect proves to be its ability to be fused without decomposition, which in conditions of the given experiments furthers the thickening of the charge, which prevents the penetration of combustion into its depth.

²Experiments were also conducted with charges of PETN, hexogen, tetryl, trotyl and amatola (80:20) with a weight of 50 grams at the increased temperatures, which lead to the spontaneous ignition (the pressure of the breaking of the shell of 500-700 at). It is obvious that at the moment of ignition the indicated explosives were in a molten state. The PETN and hexogen provided detonation; the degree of fragmentation of the shell during the combustion of tetryl was close to the detonation, and ammotol caused only the breaking of the vessel. Thus, it is obvious that the increase in temperature, in this case with the melting of explosives, increases the intensity of the combustion and its tendency toward a transition into an explosion.

A study of the combustion of powdery explosives in steel vessels allowed comparing the various explosives in the tendency of combustion toward the transition into an explosion and establish the effect of a number of factors (density, dimensions of particles, admixtures) on this transition. The main advantage of the method of the use of steel vessels is the simplicity and possibility of rapidly obtaining the characteristic of the tendency of a certain explosive toward the transition of combustion into an explosion. In essence the possibility of the obtaining of such a characteristic by so crude a method was somewhat unexpected. Apparently, distinctions between the studied explosives and the effect of their physical structure are so great that they are revealed even with this method.

The deficiency of the method is the necessity of the use of an armored chamber, designed for a rather powerful explosion and which provides the catching of metal fragments, and the use for the experiments of a considerable amount of explosives, which is also sometimes difficult. Furthermore, the method gives only the final result of the experiment and, moreover, only in a semiquantitative form (number and dimensions of the fragments) and does not characterize the development of the process with time.

The indicated deficiencies are absent in another method of the study of the transition of combustion into an explosion, which consists of the ignition of a small (1-10 grams) charge of explosives in a manometric bomb and a recording of the change in pressure with time. In essence this method is a variant of the Vieille method, developed and modernized in reference to the charge, consisting, as the rule, of one large "grain." In a somewhat different variant this method was used in the work of Gorbunov [198]; it consisted in the determining of the relative density of the powdery explosive, which separates the region of its normal combustion with increasing pressure from the region of accelerated combustion, conditioned by the penetration of combustion into the depth of the charge. In a

manometric bomb with a pressure sensor, which allows recording not only the increase, but also decrease in pressure,¹ ignited is the charge of the examined powdery explosive with a definite dimension of the particles in the form of an evenly condensed charge of definite diameter, armored on all sides except one end. At a constant weight of the charge, i.e., at a constant density of the loading, that relative density ρ_* of the explosive was determined below which the combustion passed from a normal into an accelerated mode. This transition appeared in that the curve $p(\tau)$, in the beginning of combustion coinciding with the curve for a maximally condensed charge, was deflected from it upward, i.e., in the direction of large $\Delta p/\Delta \tau$ (Fig. 194). This denoted that combustion passed from a normal mode into the mode connected with its penetration into the depth of the charge. According to the increase in the surface of combustion, the rate of the rise in pressure with time increased more rapidly. The more the critical density, the more the stability the combustion of the given explosive.

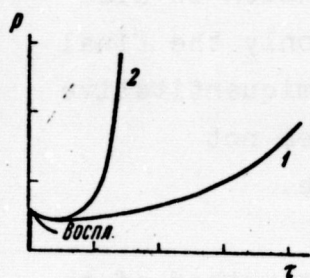


Fig. 194. Form of curve $p(\tau)$ for a maximally condensed explosive (1) and for an explosive of reduced density (2).

Воспла — curve during the combustion of one igniter.

Strictly speaking, it is more correct to characterize the stability of combustion by critical density and by critical gas permeability, which to greater extent than density, determines the possibility of the penetration of products of combustion into the depth of the charge. It is all the more expedient that, as the

¹In the indicated action a strain-gage sensor was used; it is possible and even more expedient to use a piezoelectric sensor, which allows recording of more rapid changes in pressure.

experiment indicates, for different explosives with an identical relative density (and, naturally, identical initial dimensions of the crystals) the gas permeability can be substantially different.

By comparing at the indicated identical conditions the different explosives, it is possible to establish the relative tendency of the combustion of each of them toward the transition into an accelerated mode.

It is possible to solve another problem by this method: in working with some explosive, determine the effect on the stability of the combustion of various characteristics of the charge, for example, the dimension of the particles, the relationship of dimensions of the charge, the characteristics of ignition and others. In the work of Gorbunov [198] the method was used to obtain the characteristics shown above.

We must not forget in using the given method, the known conditionality of the constancy of the density of loading in the comparison of different explosives. The direct reason for the penetration of gas products of combustion into the depth of the charge is the achievement during combustion of a definite pressure. The magnitude of the pressure at the given density of loading can greatly be distinguished for different explosives. Furthermore, under given conditions of the experiment the magnitude of pressure very greatly depends on the duration of combustion as a result of the very relatively great heat emission of gases to the walls of the bomb. Finally, curves $p(\tau)$ in the experiments of Gorbunov did not indicate the single-valued dependence of the acceleration of combustion upon the achieved pressure and why as the characteristic of the phenomenon the criterion shown above - critical density at a constant density of loading was used.

Eight explosives were studied. A charge of particles of definite interval of dimensions, chosen by sifting on sieves, was condensed in portions in a small plexiglass container with a diameter of 10 mm

and a thickness of the walls of 2 mm. The weight of the charge was usually 1 or 2 grams, and in this case the density of loading was equal to 0.02 and 0.04 g/cm³. For ignition black powder No. 3 was used.

Used the criterion of the mode of normal combustion was the independence of curve $p(\tau)$ of the length of the charge – the initial section of this curve for a large charge repeats that which an experiment with a small charge gives; in contrast to this, with accelerated combustion the curve of the large charge comparatively early starts to go higher than the curve of normal combustion.

Let us examine the general character of curves $p(\tau)$ in several typical illustrations. For trotyl (Fig. 195) with a dense charge (curve 3) after the rapid small rise in pressure created by the igniter, there follows a rather long section of slight drop in pressure, conditioned, obviously, by the fact that the increase in pressure because of normal combustion exceeds the drop in pressure due to the cooling of the gases by walls of the bomb. Subsequently, apparently, because of the fact that the surface of the walls is somewhat heated and the heat removal in them slows down, the pressure starts to increase, accelerating, inasmuch as the rate of combustion increases with pressure.

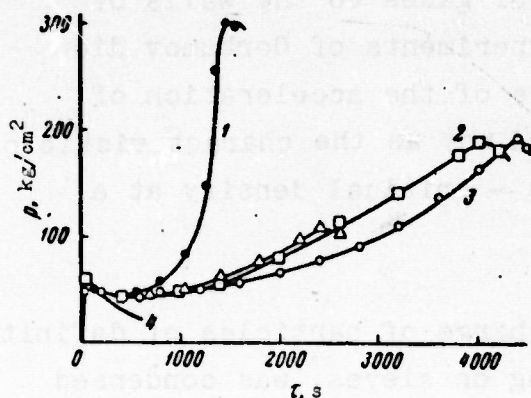


Fig. 195. Effect of density of a charge on the stability of normal combustion of trotyl. Relative density of the charge: 1 – 0.67; 2 – 0.73; 3 – 0.96; 4 – curve $p(\tau)$ during the combustion of one igniter (1.0 gram). Specific resistance in arbitrary unit: 1 – 2.5; 2 – 5.8.

If the density of the charge is somewhat less (curve 2), then in the beginning the curve proceeds just as for the maximally condensed charge; subsequently, it proceeds somewhat higher, probably, because the fusion is forced by increasing pressure into the depth of the powder, and the effective coefficient of heat transfer increases respectively..

With a considerable decrease in density (curve 1) the rapid increase in pressure approaches relatively early, and this serves as an indicator of the transition of the combustion into an accelerated mode. For some explosives (tetryl, PETN, hexogen, fulminating mercury) the acceleration of combustion occurred so sharply that it could not quantitatively be recorded by the instrument¹ used, and usually in these cases the small plexiglass vessel was crushed.

However, hexogen differs in some characteristics (Fig. 196); for a dense charge curve $p(r)$ proceeds in the beginning higher than that for a less dense charge. In the latter case, apparently, the penetration of the gases of the igniter into the depth of the charge, inadequate in order to immediately ignite it on the internal surface, leads to their powerful cooling, which is also exhibited in the lower level of pressure. After some time there approaches a steep rise of pressure. It is possible that the period of the very slow increase in pressure preceding this rise is the end combustion of the layer of explosives, fused and pressed by the gas products of combustion of the igniter; after the burning of this layer the penetration of combustion into the depth of the remaining part of the charge occurs. Indicating the validity of this explanation the nature of curves for infusible potassium picrate (Fig. 197) where the section of the slow increase in pressure is practically absent.

¹The strain-gage sensor had a frequency of natural oscillations of 18-20 kHz, and in combination with the strain-gage UTS-12k and vibrator of the oscillograph MP02 it allowed the recording of a signal with sufficient accuracy with the duration of the rise in pressure of not less than 1 millisecond.

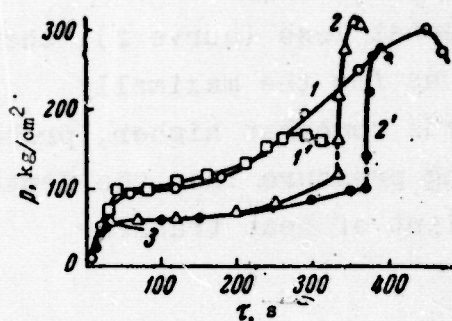


Fig. 196.

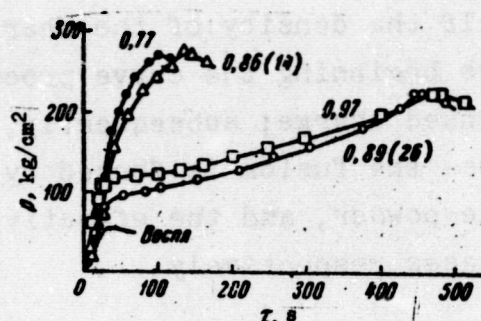


Fig. 197.

Fig. 196. Effect of the density of a charge on the stability of normal combustion of hexogen. Relative density of the charge: 1.1' - 0.98; 2.2' - 0.93. Specific resistance in arbitrary units: 2.2' - 110. Weight of the charge: 1' - 1.0 gram; 1 - 2.0 gram; 2.2' - 1.50 gram; 3 - curve $p(\tau)$ with the combustion of one igniter (1.0 gram). The dashed line denotes the transition of combustion into an explosion, which was accompanied by fragmentation of the small vessel.

Fig. 197. Effect of density of the charge on the stability of normal combustion of potassium picrate with the dimension of the particles of 50-60 μ m. Numbers near the curves denote the relative density of the charge and specific resistance (in parentheses). Weight of the charge, 2.0 gram; Воспла - curve $p(\tau)$ with combustion of one igniter (1 gram).

A comparison of the explosives studied in the relationship of the tendency of their combustion toward a transition into an accelerated mode is given on Table 29, in which the explosives are located in order of an increase of the indicated tendency. It is least of all for trotyl and xylyl,¹ and then picrates potassium, picric acid, tetryl, hexogen, PETN and fulminating mercury follow.

¹The transient region was studied insufficiently in detail in order to establish which of these two explosives should be put in first place; xylyl burns two times longer than trotyl; it is true that the magnitude of maximum pressure during the combustion of xylyl is considerably less (150-200 at), than trotyl (190-300 at).

Table 29. Initial data and results of experiments in comparison with the stability of combustion of explosives. (Weight of the igniter, 1.0 g, and diameter, 10 mm).

Explosive	Relative density	Dimension of particles μm	Height, mm weight of the charge, g	The time of a combustion, s	Maximum pressure, at	Time up to acceleration, s	Specific resistance, mm Hg/cm ³	Result of experiment	Degree of fragmentation of vessel (number of fragments)
1	2	3	4	5	6	7	8	9	10
Trotyl	0,96	50-60	15,2/2,00	4,40	192	—	—	Normal combustion	No
	0,73		20,8/2,00	4,00	190	—	5,8	The same	"
	0,67		23,0/2,00	1,46	300	0,60	2,5	Accelerated combustion	"
Xylol	0,98	50-60	15,4/2,00	8,10	162	—	—	Normal combustion	No
	0,78		19,3/2,00	8,20	150	—	—	The same	"
	0,73		20,8/2,00	2,40	175	0,70	3,0	Accelerated combustion	"
	0,63		23,5/2,00	1,60	217	0,06	—	The same	"
Potassium picrate	0,95	50-60	14,1/2,00	0,47	224	—	—	Normal combustion	No
	0,89		15,1/2,00	0,45	224	—	26	The same	"
	0,86		15,7/2,00	0,14	276	0,03	14	Accelerated combustion	"
	0,77		17,6/2,00	0,11	272	0,03	—	The same	"
Potassium picrate	0,87	20	15,5/2,00	0,47	210	—	—	Normal combustion	No
	0,84		16,1/2,00	0,46	214	—	39	The same	"
	0,81		16,7/2,00	0,16	270	0,03	17	Accelerated combustion	"
	0,81		16,7/2,00	0,16	270	—	—	The same	"
Picric acid	0,97	20	14,1/2,00	3,36	148	—	—	Normal combustion	No
	0,94		15,0/2,00	4,00	160	—	—	The same	"
	0,87		16,2/2,00	4,00	160	—	—	" "	"
	0,81		17,4/2,00	0,94	230	0,30	21	Accelerated combustion	"
	0,67		15,7/1,50	0,13	334	0,06	—	The same	"
Tetryl	0,96	50-100	15,1/2,00	1,84	230	—	—	Normal combustion	No
	0,89		16,2/2,00	1,81	230	—	—	The same	"
	0,86		16,9/2,00	0,16	327	0,03	37	" "	"
	0,83		17,3/2,00	0,07	360	0,05	—	Explosion	Up to 20
Hexogen	0,98	50-60	13,6/2,00	0,44	295	—	—	Normal combustion	No
	0,98		6,8/1,00	0,29	168	—	—	The same	"
	0,93		10,8/1,50	0,39	270	0,37	110	Explosion	10-15
	0,93		10,8/1,50	0,36	306	0,33	110	" "	10-15
PETN	0,90	10	15,1/2,00	2,25	205	0,20	—	Normal combustion	No
	0,90		7,6/1,00	1,43	96	0,06	—	The same	"
	0,82		12,6/1,50	0,74	308	—	400	Explosion	10-12
	0,75		13,9/1,50	0,08	410	—	—	" "	Up to 50
Fulminating mercury *	0,99	50-100	13,1/0,96	0,11	87	—	—	Normal combustion	No
	0,95		13,8/0,96	0,11	83	—	—	The same	"
	0,89		14,0/0,95	0,03	115	0,03	1900	Explosion	10-15

*The diameter of the charge of fulminating mercury is 4.8 mm, and the thickness of the walls of the vessel is 2.5 mm and its length, 20 mm.

The effect of dimensions of the particles (Fig. 198) consists in the fact that with the use of very fine particles, the penetration of combustion into the depth of the charge does not occur despite the relative small density (0.57); combustion occurred practically during the same time as that for the maximally condensed powder. When using large particles combustion rapidly starts in an accelerated mode; however, its intensity is less than that with the use of a certain intermediate dimension of the particles. A similar effect on the nature of the combustion is rendered by the change in density at the constant dimension of the particles; for fine particles (10 μm) even at small density (0.71) and at the considerable weight of the charge (1.5 grams), the penetration of combustion into the depth of the charge did not occur; with smaller densities it occurred and brought the acceleration of combustion up to an explosion; acceleration approached earlier when there was less density.

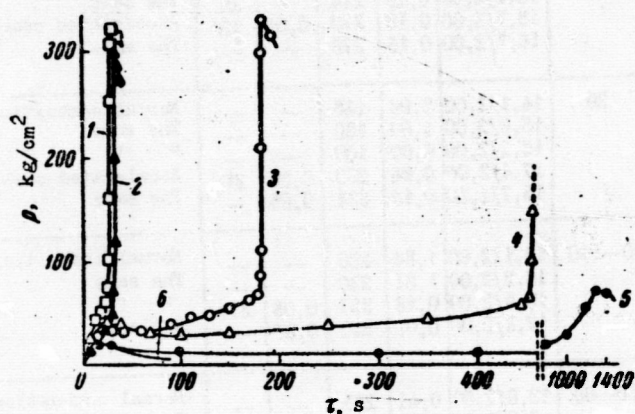


Fig. 198. Effect of dimensions of particles on the nature of combustion of PETN. The interval of dimensions of the particles in μm : 1 - 400-500; 2 - 300-400; 3 - 100-160; 4 - 63-100; 5 - 10; 6 - curve $p(\tau)$ during the combustion of one igniter (0.5 grams). For PETN with the dimension of the particles of 63-100 μm an explosion with the fragmentation of the small vessel was observed, and in all remaining experiments there was combustion without the breaking of the small vessel.

A unique effect on the transition of combustion into an accelerated mode and into an explosion is rendered by the height of the charge. The increase in height of the charge of fine-grained PETN of small density (0.25) accelerated the transition of combustion

into an explosion. At great density (0.40 and 0.58) small charges did not give an explosion; at great height of the charge an explosion approached but considerably later than that with small density. Similar experiments in the same interval of the weight of the charges but with two times greater diameter, i.e., with the smaller height of the charge, indicated a similar effect of the increase in the charge, but all the times were much less.

However, in all these experiments in essence the effect of two factors – the height of the charge and density of loading were combined. In order to divide the effect of these factors, the experiments at constant density of loading (weight of the charge) were conducted. From Fig. 199 it is evident that the charge of low height burns and great height explodes, although this explosion approaches later, the greater the height, obviously, in connection with the fact that the time of the penetration becomes more. The importance of the height of the charge is illustrated even more visually by an experiment in which a charge of definite weight was placed in two small vessels of the same diameter; an explosion did not occur, although the time up to the approach of acceleration, naturally, was somewhat shortened.

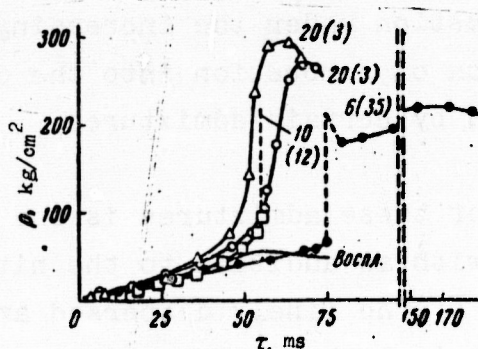


Fig. 199. Effect of height of the charge on the combustion of PETN (2 μ m) at a relative density of 0.57 and constant weight of the charge of 1.0 gram. Numbers near the curves denote diameter and height (in parentheses) of the charge in mm; Бочка – curve $p(t)$ during the combustion of one igniter (1 gram). Dashed line denotes the transition of combustion into an explosion.

If conditions for the penetration of combustion into the depth of the charge are difficult (fine particles, considerable density), then the pressure of the igniter can affect the possibility of the penetration of combustion. With a small weighted portion of the igniter combustion up to the end occurs without penetration, and at large portions the acceleration approaches earlier when the portion of the igniter is larger. However, not only the maximum pressure of the igniter, but also the speed of the rise in pressure play a role; the quick-burning igniter caused the explosion of PETN of moderate density, and possibly, this was connected with the fact that together with the igniting action it produced a certain condensation of the charge.

The acceleration of combustion and explosion approach earlier if placed under the charge in the small vessel is inert porous powder (sand), which decreases the counterpressure which appears in the depth of the charge and hinders the penetration of the gases.

The preliminary introduction of an inert gas into the bomb (50-85 at) accelerated (for PETN) the development of the process: the increase in the rate of combustion and increase in its effective temperature, apparently, prevails over the dilution of explosives by the inert gas filling the pores.

Just as with combustion under the increasing pressure of large charges, the penetration of combustion into the depth of the charge can be greatly affected by certain admixtures.

One of the types of these admixtures is the catalytic agents of combustion. Thus, with an addition to the nitroglycerine powder pulverized into powder of the finely dispersed ammonium dichromate, combustion in a manometric bomb, other conditions being equal, passed much earlier into an accelerated mode than it did in the absence of a catalytic agent (Fig. 200). The same was observed if combustion was started under increased pressure (100 at) of inert

Gas preliminarily introduced into the bomb. Experiments on combustion under constant pressure indicated that in these conditions under the presence of admixture the transition into the mode of penetration is observed at a much smaller pressure and, respectively, smaller rate of combustion than it is for powder without an admixture.

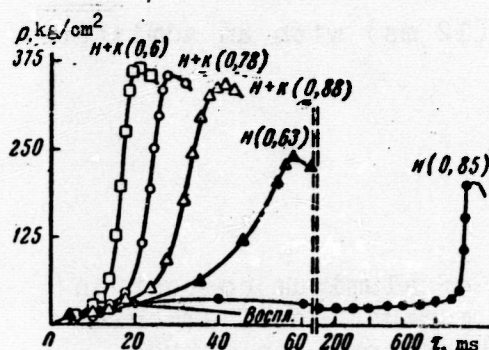


Fig. 200. Effect of ammonium dichromate (5%) on the combustion of nitroglycerine powder pulverized in a powder in a manometric bomb. Воспл - 0.5 gram of black powder; H - powder; $H + K$ - powder with dichromate. Numbers near the curves denote the relative density of the charge.

An example of the second type of admixtures can be aluminum inconjunction with ammonium perchlorate. According to experiments of V. M. Rogozhnikov, the addition of finely dispersed aluminum to ammonium perchlorate increases its ability to burn. Thus, if at 30 at the critical diameter of the combustion of perchlorate ($\rho = 1.17 \text{ g/cm}^3$) is ~ 10 mm, then in the presence of 5% aluminum it is lowered to 5 mm. With an increase in aluminum content the further not so great a decrease in the critical diameter is observed; at 25% aluminum it is ~ 3 mm. It is interesting that with an admixture of 5% aluminum the rate of combustion of ammonium perchlorate (at 50 at) not only does not increase, but even noticeably decreases, which, however, is observed also with the introduction of some organic combustible additions into the ammonium perchlorate.

In the manometric bomb the ammonium perchlorate in a small glass vessel ($d = 17$ mm) is ignited and burns with difficulty; an igniter considerable in weight is required; combustion is especially difficult with increased density of the powder.

The admixture of finely dispersed ($1\text{ }\mu\text{m}$) aluminum greatly increases the combustibility, the capacity toward combustion and its tendency toward a transition into the mode of penetration (Fig. 201).¹ The perchlorate itself under conditions of these experiments is ignited only at the two times greater weighted portion of the igniter, and the pressure reaches a maximum only after 400 ms; with a content of 27% aluminum the maximum of pressure approaches after 20 ms, and smaller contents of aluminum combustion turns into an explosion, which occurs earliest of all (12 ms) with an admixture of 5% aluminum.

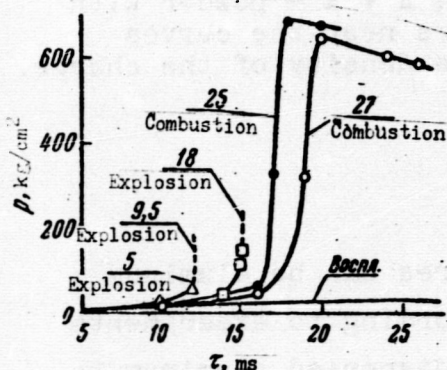


Fig. 201. Effect of aluminum content on the nature of the combustion of ammonium perchlorate. Numbers near the curves indicate the quantity of aluminum added in percent.

Just as for organic explosives, the transition of combustion into the mode of penetration of combustion into the depth of the charge furthers and accelerates its increase in height of the charge (at its constant weight). The great decrease in dimensions of particles of perchlorate (down to $10\text{ }\mu\text{m}$) delays the advance of acceleration and impedes the transition of combustion into an explosion. A similar effect is rendered by the increase in the relative density of the mixture.

¹Experiments conducted in a small vessel ($d = 15\text{ mm}$, $m = 3\text{ g}$, $\rho = 1.1\text{ g/cm}^3$, igniter - 0.5 g of smoky powder, $p_{\text{воспл}} = 30\text{ ат}$).

With the ignition of the mixture by the igniter placed in the bottom part of the small vessel (in order to eliminate the effect of the penetration of combustion), the acceleration of gasification proceeded faster, but its rate did not reach explosive values. At a pressure of up to 300 at the rates of combustion of the perchlorate with aluminum and without it are similar; above 300 at an intermixture burns faster. At a content of 25% aluminum the rate of combustion is considerably greater than it is at 5%; with "end" combustion the relationship of the times of combustion and tendencies toward its transition into an explosion was the opposite.

With combustion over the entire surface of the cylindrical charges of great density under a pressure of up to 350 at the perchlorate burned faster than its mixture with 5% aluminum.

Experiments of V. V. Gorbunov on the addition of aluminum to nitrocellulose (the pyroxylin No. 1) indicated the effect opposite to that which was observed in the case of ammonium perchlorate — a noticeable retarding of the increase in gasification, especially expressed with increased density of the mixture.

From the totality of obtained data it follows that aluminum in small contents greatly facilitates the transition of the combustion of ammonium perchlorate into a convective mode. The most probable reason for this effect should be seen in the interaction of aluminum with the initial products of the dissociation of ammonium perchlorate; in this case as a result of the great thermal effect of oxidation of the aluminum gases with a high temperature are formed, which, in penetrating into the powder, ignite its particles much easier than the relatively cold products of dissociation of the perchlorate itself do. Judging from the fact that the most effective proves to be small in comparison with stoichiometric content of aluminum, the question is about its interaction with the small quantity of the products of dissociation of perchlorate, separable by the surface

layers of the particles. The excess in aluminum not only does not help the penetration of combustion into the depth of the charge, but even impedes it, part of the heat is consumed since for the heating of this excess. The decisive role of the penetration of combustion is emphasized by the fact that aluminum does not increase the rate of the normal combustion of ammonium perchlorate. It is no wonder that aluminum does not intensify the combustion of pyroxylin; the combustion of the latter forms the products comparatively poor in oxygen and less reactive than in the case of ammonium perchlorate. Even in the combustion of ammonium nitrate the effect of aluminum on this transition is much weaker.

VI. The Combustion of Heterogeneous Systems

1. Mechanism of Combustion

Leypunskiy [199] examined the mechanism of combustion of a heterogeneous system in which the components (fuel and oxidizer) are contained in the form of macroscopic particles, and one of them has low vapor pressure. These conditions are fulfilled, for example, in the combustion of black powder especially in its sulphur-free variant. In this case a reaction cannot occur in the gas phase and should occur on the surface of particles of a nonvolatile component (a carbon).

The following sequence of processes during the combustion of black powder is taken: the saltpeter is decomposed, liberating the oxygen, which by diffusion in the gas phase proceeds to the particle of the carbon, reacts on its surface, and products of reaction also by diffusion in the gas are removed from the carbon particle. A substantial side of the mechanism of combustion is the dependence of the rate of the elementary act of the combustion - the combustion of the carbon particle - upon pressure.

In the kinetic region the rate of combustion of carbon is proportional to the pressure of the oxygen. In a diffusive region, when the reaction of carbon with oxygen occurs so rapidly that the rate of diffusion limits the rate of combustion, the time of combustion of the carbon particle will depend on the conditions of diffusion. Let us assume that q_0 is the quantity of oxygen necessary for the combustion of the particle of carbon of the considered dimensions, D - the coefficient of diffusion ($\nu \frac{1}{p}$), C_0 - the concentration of oxygen at infinity (νp), $r_{\text{эфф}}$ - effective means of diffusion (the gradient of concentration is equal to $C_0/r_{\text{эфф}}$), τ - the time of combustion of the particle and S - its surface. Then

$$q_0 \approx D \frac{C_0}{r_{\text{эфф}}} \tau S \quad (3.33)$$

and

$$\tau \approx q_0 \frac{r_{00}}{DSc_0} \quad (3.34)$$

The denominator in expression (3.34) does not depend on pressure, and q_0 also does not depend on it. The dependence of the time of combustion of the particle upon pressure will be determined by the dependence upon pressure of the effective means of diffusion. With the combustion of a carbon ball in the atmosphere of oxygen, the effective means of diffusion is equal to the radius of the ball, i.e., does not depend on pressure; correspondingly the time of combustion of the carbon ball does not depend on the pressure of the oxygen. The same can occur if the source of oxygen (particle of saltpeter) and a carbon particle are in a solid phase at an invariable distance from each other. With the combustion of a flat plate the means of diffusion is equal to the thickness of the layer of oxygen necessary for the combustion of the plate. The thickness of this layer is $\sim \frac{1}{p}$; therefore, the time of combustion will be inversely proportional to the pressure of oxygen. Thus, the time of combustion of the carbon particle can, with an increase in pressure, decrease or remain invariable depending on external conditions.

Inasmuch as saltpeter is decomposed at a relatively low temperature at which, as Leypunskiy proposed, the combustion of the carbon still does not occur, then gas products of the dissociation of saltpeter should take away the unburned particles of carbon, which react in a gas-carbon flame over the surface of the powder. Thus, the case of the combustion of a carbon ball in the atmosphere of oxygen, when the time of combustion does not depend on pressure, is carried out.

The rate of the propagation of the flame in a carbon-air mixture is from 10 to 50 cm/s, which corresponds to the rate of consumption of carbon of $3.3\text{--}11 \text{ mg/s}\cdot\text{cm}^2$, and in the recalculation for the rate

of combustion of powder, 0.015-0.05 cm/s. This magnitude is considerably less than the rate of combustion of black powder (1 cm/s); however, the difference, nevertheless, does not exceed 1-2 orders.

The independence of the time of combustion of the particle of carbon upon pressure does not denote the absence of the dependence of the rate of combustion upon pressure. According to the theory of Zeldovich, the linear rate of the gasification of powder is proportional to the square root of the magnitude of the rate of the volumetric heat release in the zone of the reaction. In the combustion of black powder, with an increase in pressure proportionally to it the quantity of carbon and oxygen per unit volume and, respectively, the volumetric rate of the heat release increase. Thus, the considered scheme of the combustion of black powder is formally similar to the scheme of the combustion of smokeless powder. The burning particles of carbon are similar to the large molecules reacting according to a monomolecular law; the carrying away of the carbon in the flow corresponds to gasification, and the heat necessary for the dispersion of the powder and the preparation of an ignitable mixture is fed from the gas phase. The rate of combustion should in such case increase in proportion to the square root from the magnitude of pressure in accordance with the quasi-monomolecular law of reaction.

Another course of reasoning relative to the dependence of the rate of combustion upon pressure with independence of it of the rate of combustion of an individual particle is based on the investigation of the layer of the burning gas-carbon mixture, characterized by a definite depth of burning, i.e., by the definite time of combustion. With the increase in pressure the linear rate of the flow of gases decreases proportionally, and since the time of combustion of the particle does not depend on pressure, then the distance from the surface on which there will be burning dust

particles and hot products of combustion of the examined layer is decreased, and the temperature gradient, which determines the flow of heat to the surface of the powder, respectively, will increase in proportion to the pressure.

The increase in the temperature gradient in the considered layer of the burning gas-carbon mixture will not lead to its cooling because the concentration of the gas-carbon mixture, i.e., the volume rate of the liberation of heat will increase in proportion to pressure. Therefore, the temperature of the examined gas layer will be invariable, and only it will move toward the surface. The increase in the temperature gradient will lead to the increase in the flow of heat to the surface of the powder, i.e., to the increase in the rate of gasification.

From the equality of the quantity of heat fed from the region of reaction and that being consumed with the gasification of the powder:

$$V_K \rho_K (T_n - T_0) c_K = \eta \frac{T_{\text{эфф}} - T_n}{X_{\text{эфф}}} = \eta \frac{T_{\text{эфф}} - T_n}{V_r \tau_{\text{эфф}}}, \quad (3.35)$$

$$V_r \rho_r = V_K \rho_K.$$

where V_K , ρ_K , c_K - the rate of gasification, density, heat capacity of the condensed phase; T_0 , T_n , $T_{\text{эфф}}$ - initial temperature of the powder, temperature of the surface of the powder, and the effective temperature of the region of the reaction adjacent to the surface of the powder and determining the heat transfer to the surface; $X_{\text{эфф}}$ - distance from the surface to the region in the gas with temperature $T_{\text{эфф}}$; $\tau_{\text{эфф}}$ - time of combustion of that quantity of carbon which is necessary for the achievement of temperature $T_{\text{эфф}}$; η - coefficient of thermal conductivity

$$(V_K \rho_K)^2 = \frac{\eta}{c_p} \frac{T_{\text{эфф}} - T_n}{T_n - T_0} \frac{\rho_r}{\tau_{\text{эфф}}}. \quad (3.36)$$

Since with an increase in pressure not only the temperature gradients but also the volume rates of the liberation of heat will increase proportionally, then $T_{\text{эфф}}$ should not be changed with an increase in pressure. Since T_n depends little on pressure, and η and $T_{\text{эфф}}$ do not depend on pressure, then according to equation (3.36)

$$V_{\text{нрн}} \sim \frac{\sqrt{p_r}}{r} \sim \frac{\sqrt{p}}{r}, \quad (3.37)$$

i.e., the rate of combustion is proportional to the square root of the magnitude of pressure. If the combustion of particles of carbon occurs in a dynamic region, then the rate of reaction on the surface of the carbon is proportional to p^n , where $0 < n \leq 1$. Respectively, the rate of combustion of the particles $\tau \sim r/p^n$; then, according to equation (3.36)

$$V_{\text{нрн}} \sim \sqrt{\frac{p_r}{\tau_{\text{эфф}}}} \sim \sqrt{\frac{p^{1+n}}{r}}. \quad (3.38)$$

i.e., the rate of combustion is proportional to the pressure to the power $(1 + n)/2$ and is inversely proportional to the root of the radius of the particle.

Thus, with the combustion of carbon in the dynamic region the rate of combustion of the powder depends more greatly on pressure than that with combustion in a diffusive region, and it can be proportional to pressure (when $n = 1$).

The dependence of the rate of combustion upon the dimension of the particles in a kinetic region is weaker than that in a diffusive region.

A more accurate calculation of dependence $u(p, r)$ for the examined scheme of combustion was conducted by Novozhilov [200], taking into account, specifically, the fact that the rate of the motion of particles of carbon can be less than the rate of the motion of the gas. With a number of assumptions he arrives at the conclusion that the limit of the diffusive and dynamic conditions should lie at about 1 at; lower than this pressure, i.e., during combustion in a dynamic mode, the rate should increase in proportion to the first power of pressure, and at high pressures in a diffusive mode, proportional to the cubic root of pressure. The absolute magnitude of the rate, according to calculation, should be ~ 1 mm/s.

With the further refinement of the theory [201], besides a more correct account of the diffusion of the oxidizer and forces acting on the particle which moves in the gas, it was taken into account that the inflammation of the particle of carbon occurs not immediately after it is detached from the surface of the powder but only when the temperature of the surrounding gas achieves a certain ignition temperature. The calculation estimate of this temperature in reference to black powder indicates that it is significantly higher than the temperature of the surface taken equal to 300°C . Calculation gives for the rate of combustion the expression $n \approx \frac{10^{-5}}{d} p^{1/2}$. When $d = 10^{-3}$ cm we obtain for air pressure $u = 10^{-2}$ cm/s, i.e., three orders less than the experimental value of the rate of combustion of black powder.

This nonconformity leads the author to the conclusion that the actual scheme of combustion should include ignition of the particle considerably earlier than temperature of its ignition will be achieved in the gas phase, possibly, on the surface of the solid phase, and the temperature of the particle will be higher than the temperature of the surrounding oxidizer; in the gas phase the after-burning of the fuel will occur. The reaction which determines the rate of combustion will occur not in the gas but in the condensed phase.

Novozhilov [202] also examined the combustion of the powder mixture, both components of which are able to be gasified in diffused and kinetic regions. Figure 202 depicts the diagram of combustion for a diffusive case. The powder consists of layers of substances *A* and *B* of identical thickness $2h$; if the components are identical in their physical features and the rate of chemical dissociation equally depends on concentration *A* and *B*, the pattern of combustion will be periodic in space with period $2h$. In order to find the rate of combustion of such a powder, it is necessary to examine the elementary cell limited by planes *MN* and *PS*. Obviously, the maximum of the heat release will be located on a line Ox ; in connection with this the flow of heat from the gas phase to the surface of the solid phase will not be evenly distributed on the surface of the latter. This conditions the nonuniform burning of various parts of the surface, and burning powder will have a surface similar to that shown on Fig. 202.

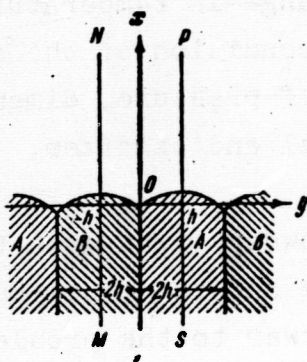


Fig. 202. Diagram of the combustion of a powder mixture *A* and *B* — layers of substance of identical thickness.

To simplify the problem it is assumed that the surface of the powder is flat and coincides with plane $x = 0$. Further it is admitted as a maximum case that the rate of chemical dissociation is infinite, and, respectively, the rate of combustion is limited by the rate of diffusion. In this case the zone of chemical reaction will be infinitesimally thin: it will coincide with the plane $y = 0$.

Furthermore, the concentration of reactive substances in the zone of reaction will be equal to zero. Plane y behaves as an absolutely absorbing surface, and it separates the region $y < 0$, where there is substance B and products of reaction C and D and no substance A , from the region where there is A , C and D and no B .

The mathematical examination of this case indicates that for it the rate of combustion does not depend on pressure and is inversely proportional to dispersity. When the ratio of the rates of diffusion to the rate of chemical reaction is great and the limiting process is the chemical reaction, the rate of combustion is proportional to the pressure and (if the reaction is bimolecular) does not depend on dispersity.

*Theory of the combustion powder mixtures
of Summerfild*

Summerfild, Sazerland, Webb, Toback and Hall [203] [Translator's Note: spelling not verified] propose the physicochemical model of the zone of combustion, which describes the change in temperature, the rate of reaction, diffusive processes and condition of the gas flow, which would allow predicting the effect of pressure, dimensions of the particles and the relationship of the fuel and oxidizer.

The object of the investigation was the powder mixture on the basis of finely pulverized ammonium perchlorate and the copolymer ester-styrene. Experiments should give the answer to the problem about whether or not on the surface there is a liquid layer of an oxidizer or fuel. In a positive case the gases, being formed by the fuel and oxidizer, can enter into the zone of the gas-phase reaction, being partially mixed and vice versa. The second problem, which is connected with the first, is whether mixing occurs by means of molecular or turbulent diffusion.

Photographs of combustion in its own light emission, and also schlieren photographs indicate that in a thin (1 mm) bed adjacent to the surface there is no turbulence; than nonuniformity which was revealed with colored high-speed filming and with the measurement of temperature should be attributed to vibrations in the degree of mixing in the reaction layer. Microphotographs in passing light, which indicate the notched profile of the surface of combustion, point to the fact that fusion on it does not occur. This is confirmed by a comparison with the combustion of the composition on the basis of potassium perchlorate, the product the decomposition of which (KCl) is melted before vaporization, which leads to a level surface with bubbles breaking through it.

The measurement of the temperature by thin platinum-rhodium thermoelectric couples and also the measurement of the radiation of the flame indicated that at pressures above 14 at the thickness of the reaction zone is less than 100 μm , assuming that the temperature of the surface is equal to 700-800°C. The last method indicates also that the zone of the flame is microheterogeneous, and the scale of the heterogeneity is at least equal to 10 μm . Information on the chemical nature of particles which are formed in the flames was obtained by the spectroscopic method.

The investigation of experimental data leads to the following presentation about the mechanism of combustion. A quasi-stationary gaseous flame is adjacent to the surface, as is shown on Fig. 203. The surface is dry, i.e., gases formed by an oxidizer and fuel, are liberated directly by the solid phase as a result of a sublimation or of pyrolysis. The mixing of the fuel and oxidizer occurs only in the gas phase. In the solid phase there does not occur any reactions which would affect the flame, and heat is not liberated. Reactions of sublimation or pyrolysis on the surface can be exothermic or endothermic. As a result of oxidizing reactions the heat is liberated in the thin reaction zone in the gas phase.

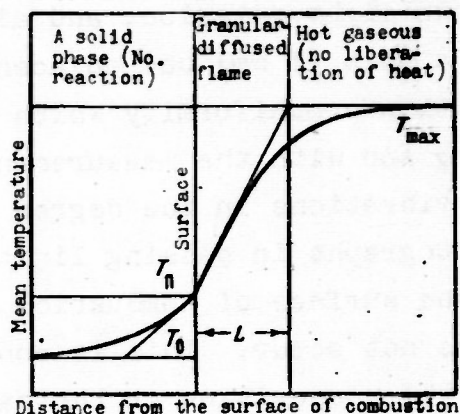


Fig. 203. Theoretical model of the steady zone of flames with a temperature profile average in time.

Vapors of the fuel or oxidizer are liberated in the form of the individual bubbles, which then burn in the atmosphere of another component. Each bubble on the average is less in mass than the individual crystalline particle of the oxidizer, but nevertheless their masses are found in a certain dependence — the larger the crystal, the larger the bubble. It is assumed that the mass of the bubble does not depend on pressure. Bubbles passing through the zone of the flame gradually react with the rate being determined by diffusive mixing and kinetics, liberating heat. This structure of the zone of the flame is called bubble-diffusion.

The physical basis of the formation of such bubbles and, specifically, the independence of their magnitude of pressure is unknown; it is most probable that they are bubbles of gasified fuel which are captured by the flow of products of the gases, which were formed from the oxidizer. The propagation of combustion occurs as a result of the transfer of energy from the zone of flames to the surface of the powder, which is carried out predominantly by thermal conductivity.

Given below is the quantitative formulation of the examined concepts.

The quantity of heat necessary for initial heating of the powder from T_0 to T_n is transmitted by the exothermic reaction of the gasification of its components and by the thermal conductivity in the gas phase with a mean temperature gradient.

$$\frac{T_1 - T_n}{L}, \quad (3.39)$$

$$u_n [c_s (T_n - T_0) - Q_s] = \lambda_{gs} \frac{T_1 - T_n}{L}, \quad (3.40)$$

where u_n - mass rate of combustion; c_s - heat capacity of the powder, T_n - some mean temperature of its surface; T_0 - initial temperature; Q_s - positive thermal effect of the gasification of powder components; λ_{gs} - coefficient of thermal conductivity of gases near the surface of the powder; T_1 - the final temperature of combustion; L - thickness of the zone of combustion.

The linear rate of pyrolysis of both components can be expressed by the relation

$$u_n = B \exp(-E/RT_n). \quad (3.41)$$

With stationary combustion both rates are equal to each other (and the rate of combustion of the powder).

Inasmuch as the energies of activation of pyrolysis of the oxidizer and fuel are different, the temperature on the surface of their particles should be different. Therefore, the concept of mean temperature is a certain arbitrary approach. This temperature is assumed to be independent of pressure, dimensions of the particles and the ratio of the oxidizer and fuel, but one should expect that it depends on the copper chromite content, which is the catalytic agent of the decomposition of perchlorate.

For the determination of the thickness of the zone of reaction L , two maximum cases are considered. At very low pressures the rate of the molecular diffusion is much more than the rate of the reaction of the oxidation, so that the latter occurs in the mixture of the gases. At very high pressures the rate of the chemical reaction is so great that the rate of combustion is completely controlled by mutual diffusion. An intermediate case is actually possible also.

At low pressures the flame can be considered as a flow at the rate of u_M/ρ_g , in which reactions of the second order occur. Then

$$L = \frac{u_M}{\rho_g} \frac{1}{\left(\frac{d\epsilon}{dt}\right)_{cp}} = \frac{u_M}{\rho_g} \frac{1}{(1-\epsilon)^2 \rho_g A \exp\left(-\frac{E}{RT_g}\right)}, \quad (3.42)$$

and ϵ , $d\epsilon/dt$, ρ_g , etc., denote their mean values. Substituting equation (3.42) into (3.40), it is possible to find

$$u_M^2 \approx \frac{\lambda_g \rho_g (T_1 - T_n) A \exp(-E/RT_g)}{c_s (T_n - T_0) - Q_s}. \quad (3.43)$$

Thus, the rate of combustion is proportional to pressure to the first power. The thickness of the reaction zone is inversely proportional to pressure

$$L \approx \frac{\lambda_g^{1/2}}{\rho_g} \frac{(T_1 - T_n)^{1/2}}{[c_s (T_n - T_0) - Q_s]^{1/2}} \cdot \frac{1}{[A \exp(-E/RT_g)]^{1/2}}. \quad (3.44)$$

For the second maximum case under the assumption that on the surface bubbles of fuel with mass μ and dimension d are formed

$$\rho_g d^3 = \mu = \frac{P}{R_g T_g} d^3. \quad (3.45)$$

The duration of the life of a bubble is determined by the rate of gas diffusion inside and outside it.

Let us designate by letter D the coefficient of diffusion identical for both gases and averaged over the reaction zone. Then the thickness of the zone and the rate of combustion can be calculated in the following manner:

$$\tau \approx \frac{a^2}{D_g}; \quad L \approx \frac{u_m \mu^{1/2}}{\rho_g^{1/2} D_g};$$

$$u_m^2 \approx \frac{\lambda_g \rho_g^{1/2} D_g (T_1 - T_n)}{\mu^{1/2} [c_s (T_n - T_0) - Q_s]}; \quad (3.46)$$

$$L = \frac{\lambda_g^{1/4} \mu^{1/2} (T_1 - T_n)^{1/2}}{D_g^{1/2} \rho_g^{1/2} [c_s (T_n - T_0) - Q_s]^{1/2}}. \quad (3.47)$$

It is evident that the mass rate of combustion is proportional to the pressure to the 1/3 power, which agrees with observations made for powder on the basis of ammonium perchlorate.

For the intermediate case it is possible to allow that the thickness of the zone is changed partly with pressure in such a way as if it were controlled by kinetics, and partly as if it were controlled by diffusion

$$L \approx z_1 L_1 + z_2 L_2, \quad z_1 \approx 1, \quad z_2 \approx 1.$$

$$L = \left[\frac{\lambda_g (T_1 - T_n)}{c_s (T_n - T_0) - Q_s} \right]^{1/2} \left\{ \frac{z_1}{\rho_g [A \exp(-E/RT_g)]} + \frac{z_2 \mu^{1/2}}{D_g^{1/2} \rho_g^{1/2}} \right\}. \quad (3.48)$$

This expression for the thickness of the zone can be introduced into the expression of the energy balance, and for the rate combustions we obtain

$$\frac{1}{u_m} \approx \left\{ \frac{\rho_g [c_s (T_n - T_0) - Q_s]}{\lambda (T_1 - T_n)} \right\}^{1/2} \left\{ \frac{z_1}{\rho_g [A \exp(-E/RT_g)]} + \frac{z_2 \mu^{1/2}}{D_g^{1/2} \rho_g^{1/2}} \right\}. \quad (3.49)$$

Hence the dependence of the rate of combustion upon pressure is obtained in the form of

$$\frac{1}{u_n} = \frac{a}{p} + \frac{b}{p^{2/3}}. \quad (3.50)$$

This dependence makes it possible to verify the theory by means of a comparison with it of the experimental dependence of the rate of combustion upon pressure in the wide interval of the latter. At the same time the parameter of the rate of the reaction a should be a very perceptible to the temperature of the flame, and the parameter of diffusion b should be perceptible to the average dimension of the particles. Catalytic agents of decomposition increase the rate of decomposition, lowering T_n and, respectively, decreasing a and b in an identical amount.

To check the theory in the bomb of constant pressure by the method of melting of the wires passed through the charge, the rate of the combustion at pressures of 1 to 106 at was determined. The accuracy of the determination was $\pm 3\%$ and basically depended on the nonuniformity of combustion of the powder, conditioned by its heterogeneity and irregularity of the restrictor.

The obtained data in coordinates $p/u-p^{2/3}$ on a graph give straight lines (Fig. 204), and for coarse-grained perchlorate (an average dimension of 120 μm), fine-grained (16 μm), "cold" mixture (75% oxidizer) and "hot" mixture (80% oxidizer) the following values of a and b are obtained:

	a	b
1 - "cold" mixture (coarse-grained oxidizer)	365	39.0
2 - "cold" mixture (fine-grained oxidizer)	400	19.8
3 - "hot" mixture (coarse-grained oxidizer)	245	27.0
4 - "hot" mixture (fine-grained oxidizer)	160	17.3

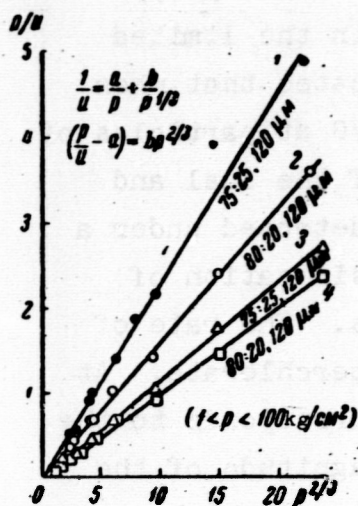


Fig. 204. Comparison of data of Suterland on the rates of combustion with the theory of Summerfield (straight lines) 1 - $b = 6.25$; $a = 9.9$; 2 - $b = 4.5$; $a = 4.35$; 3 - $b = 3.2$; $a = 10.8$; 4 - $b = 2.7$; $a = 6.6$. The ratio between the oxidizer and fuel and the dimension of their particles are indicated by numbers of curves.

Thus, both parameters are changed depending on the dimension of the particles in accordance with the theory.

The repeated determinations of the rate of combustion at different pressures produced by a different investigator gave results, which agree with those given above. However, the effect of the ratio of the oxidizer and fuel on a , which was obtained earlier and is provided also by the theory, is not revealed; at this value a is substantially less. The introduction into the powder of copper chromite decreases a and b at an identical number of times, as one would expect according to the theory.

Thus, the simple concept, which consists in the fact that in the region of the low pressures the rate of combustion is determined by the rate of the chemical reaction and in the region of high pressures by the rate of diffusion, is confirmed by that fact that the dimensions of the particles of the oxidizer do not affect the rate in the region of low pressures, and they obtain a decisive value in the region of high pressures.

The latest experiments produced, besides with the copolymer of ester-styrene, with polysulfide and epoxyresins (in the limited interval of the dimension of the particles), indicated that when using polysulfide of fuel and at pressures above 70 at particles of perchlorate are pyrolyzed much faster than that of the fuel and leave on the surface small notches, which can be detected under a microscope on extinguished charges. Thus, the gasification of perchlorate is the leading one in these conditions. The rate of combustion is close to the rate of combustion of perchlorate. At low (<35 at) pressures the state of the surface corresponds to the theory described above; this refers also to the magnitude of the rate of combustion. Deviations from the theory disappear when mixtures of two fractions of the oxidizer are used, or when mixtures with a large content of oxidizer are used.

Subsequent investigations were for the purpose of refining the role of the transfer of heat in the reaction zone by radiation, the connection between dimensions of particles of the oxidizer and parameter b , and also the conformity between the value of the rate during combustion of a cylindrical charge from the end and its value during combustion of a charge in a rocket chamber along the channel.

The rate of end combustion was determined in a bomb of constant pressure with the transmission of nitrogen flow, which emerged into the "tube" located over the charge. At rates of nitrogen in the tube from 18 to 61 cm/s at 35 at, the effect on the rate of combustion was not revealed; an admixture of up to 20% oxygen also does not change the rate of combustion. At 7 at the presence of a restrictor also had no affect. A charge with a diameter of 11.2 mm burned at 35 at 3% more rapidly than that with a diameter of 6.4 mm.

Measurements of the rate of combustion of the charge of powder with a central channel along this channel in the direction toward the periphery of the charge gave values of the rate of 7% smaller than those during end combustion ($d = 6.4$ mm), in contrast to what could

have been expected; the reasons for this distinction have not been clarified.

The measurement of the radiation of the flame and calculation of its effects indicated that it increases the rate insignificantly - 1% during combustion of a charge on the end and 6% during combustion of a charge along the channel. The intensity of radiation becomes more with an increase in the dimension of the particles; this effect appears at low pressures and is absent at high pressures.

A more specific pattern of the process of combustion is examined by Chayken and Andersen [204]. They proceed from the two-temperature postulate of Shulitz and Decker [Translator's Note: names not verified], in accordance with whom the decompositions of the solid oxidizer and binder are in microscopic scale independent processes. Linear rates of the pyrolysis of the oxidizer and fuel are equal to each other and to rate of combustions of the powder.

The linear rates of pyrolysis can be determined by the method of the hot plate; their values at different temperatures for a number of substances are given in Fig. 205. These rates for both basic components of the powder at the given temperature can be identical. Hence the conclusion is drawn that, correspondingly, there should be unequal temperatures on the surface of the particles.

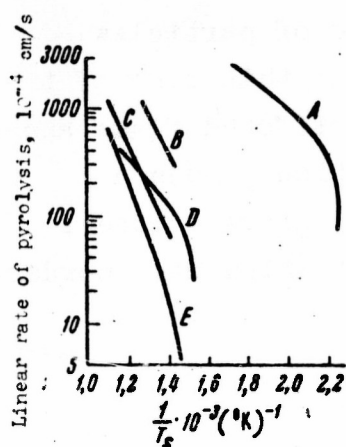


Fig. 205. Examples of linear rates of pyrolysis for some oxidizers and binders. A - ammonium nitrate; B - polystyrene; C - ammonium perchlorate; D - rubber GRS-32; E - plastic GS-2.

For powder mixtures on the basis of the ammonium nitrate, according to this hypothesis, the following stages of the process are assumed:

a) gasification of the oxidizer, the rate of which is determined by the process, which includes the endothermic reaction of desorption from the surface;

b) gas-phase reduction-oxidation reaction of products of pyrolysis of the oxidizer, which forms a flame with a temperature of about 1250°K;

c) endothermic pyrolysis of a binder in the flame;

d) gas-phase exothermic reactions between products of pyrolysis of the binder and of oxidizer.

A flame from stage 6 forces the particles of the binder to be gasified, and at a certain distance from the surface of the condensed phase between the gaseous products of the conversion of the oxidizer and binder a diffusive flame appears. However, only a small part of the heat which is liberated in this flame is transferred to the condensed phase.

It has been established, for example, that the changes, 10-100 times, of the rate of pyrolysis of the polystyrene binder do not affect the rate of combustion of the appropriate powder on ammonium nitrate. This indicates the fact that the surface of particles of the oxidizer obtains heat predominantly from the thin zone of the gas-phase reaction between NH_3 and HNO_3 , and the diffused flame appears too far in order to affect the rate of the combustion. Such a conclusion is confirmed by that fact that ammonium nitrate itself (with a catalytic agent) burns at the same rate at which many powders having it as a base burn.

The application of the simple scheme of the process, founded upon two-temperature postulate, to powder on the basis of ammonium perchlorate is complicated by certain facts.

With the combustion of powder on the surface of the oxidizer there initially occurs dissociation to NH_3 and HClO_4 (sublimation). These products react near the surface, forming a reduction-oxidation flame, as in the case of the ammonium nitrate. However, characteristics of the surface decomposition of perchlorate and nitrate are different, and there is no complete analogy in processes of the combustion of powder on their basis. In the first place, during the combustion of ammonium perchlorate, besides sublimation, on the surface an exothermic reaction in the solid phase is possible owing to the thermal effect of which the endothermicity of sublimation decreases.

The specific weight of the solid-phase reaction depends, specifically, upon the rate of combustion. In the second place, the temperature of the surface of the oxidizer during the combustion of perchlorate powders is much higher than that of ammonium nitrate powders and is close to the temperature of pyrolysis of the binders. This fact affects the degree of interaction of the oxidizer and fuel near the surface of the powder.

During the combustion of ammonium nitrate powders, if the transfer of heat in the reaction zone near the particle is carried out by thermal conductivity, and there is a linear change in temperature in it, the thickness of the zone can be approximately expressed by the relation

$$\delta = r_0(1 + r_0/\sqrt{\pi K \tau})^{-1}, \quad (3.51)$$

where r_0 - the average radius of the particle; K - the average thermal conductivity of the gas phase; τ - the period of the half-conversion of the reduction oxidation reaction in the gas phase.

Value δ is connected with the rate at which gas is expanded and with the rate of reactions occurring in it.

$$K = M\sigma/c_p\rho_g \quad (3.52)$$

where M - the mean molecular weight of the gases; σ - their mean thermal conductivity; ρ_g - density; c_p - mean molecular heat capacity. Hence it follows that the thickness of the reaction zone depends on pressure.

For the reduction-oxidation reaction of the second order in gases

$$\tau = 1/c_g k_g = 2M/\rho_g k_g \quad (3.53)$$

where c_g - concentration of one of the agents; k_g - constant of the rate

If the law of ideal gases is fulfilled, then, using equations (3.52) and (3.53), we obtain

$$\delta = \frac{r_0}{1 + \frac{r_0}{R_g T_g} \left[\frac{c_p k_g}{2\pi^3} \right]^{1/2} p} = \frac{r_0}{1 + \varphi_p}, \quad (3.54)$$

where R_g - gas constant; T_g - temperature at which the basic mass of the gas reacts; p - pressure. At a constant dimension of the particles ϕ can be considered constant.

Equating the rate of heat removal in the depth of the particle to the rate of the transfer of heat necessary for the providing a stationary state of pyrolysis on its surface, we obtain

$$4\pi nr_0^2 \frac{T_1 - T_{s,0}}{\delta} = 4\pi nr_0 \Delta H B_0 \quad (3.55)$$

where ΔH - endothermicity of the reaction of pyrolysis on the surface of the oxidizer (cal/g·mole); ρ_g - the density of the oxidizer (g/cm³); n - portion of the open surface of the particle; B_0 - the linear rate of pyrolysis of the oxidizer.

From equations (3.40), (3.54) and (3.55) we obtain the rate of combustion

$$B_p = \frac{\sigma(T_1 - T_{s,0})}{\rho_g \Delta H r_0} (1 + \varphi p); \quad (3.56)$$

$$B_p = A_{s,0} \exp(-E_{s,0}/RT_{s,0}). \quad (3.57)$$

The rate of the gas-phase interaction between NH_3 and HNO_3 is supposedly determined by the reaction



Taking part in it, NO_2 is formed as a result of the relatively rapid decomposition of HNO_3 .

Effect of a binder on the reaction zone

Concepts on the two-stage process of the conversion of the particle of the substance are added to the one-component powder. However, they are valid during the combustion powder mixtures on the basis of ammonium nitrate. The temperature on the surface of particles of the oxidizer is low ($\sim 600^\circ\text{K}$) in comparison with the temperature on the surface of particles of fuel ($\sim 1100^\circ\text{K}$). Because of this the gasification of the fuel occurs relatively far from the surface of the particles of the oxidizer and the interaction of

products of gasification – even further, and its heat does not affect the general flow of the process.

During the combustion of powder on the basis of ammonium perchlorate the temperature on the surface of particles of the oxidizer above ($\sim 1100^\circ\text{K}$), the possibility of the interaction of products of its gasification with fuel and of the effect on the process in the reaction band of oxidation is greater. This effect can be different (Fig. 206).

1. The gasified fuel can diffuse into the reaction zone but not to react in it. In this case it proves to be a diluting action, increasing the duration of the reduction-oxidation reaction δ and lowering the temperature of conversion of the oxidizer.

2. With diffusion proceeds a relatively slow interaction, and the reduction-oxidation reaction will be delayed, δ will be thicker, but a final temperature T_f will be higher.

3. With diffusion of the fuel on the outside the reaction occurs rapidly. Then the thickness of the layer remains fixed, but the temperature rises.

4. Finally, with the diffusion of fuel from without into the reaction zone the interaction does not occur – the thickness of the zone will not be changed; however, the dilution of the flame zone, i.e., a depression T_f , can take place.

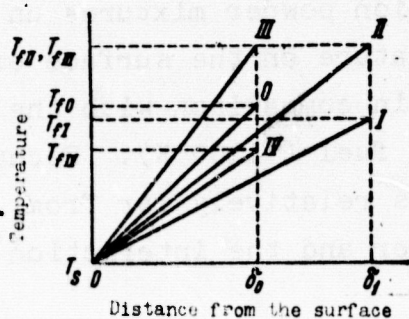


Fig. 206. Effect of a binder on a thermal layer

$$\delta_0 = \frac{r_0}{1 + \frac{r_0}{\gamma \pi k r_0}}$$

Finally, with the diffusion of fuel into the reaction zone and with its interaction at a rate higher than the rate of the reduction-oxidation reaction, the thickness of the reaction zone will depend on the rate of the diffusion reaction between the fuel and oxidizer.

The quantitative analysis of all the enumerated possibilities is a very complex task. The characteristics of the second case, apparently, the most widespread, are: a) the appearance of nonreacting fuel in the reaction zone, which leads to a decrease in the concentration of reagents and increases the duration of the reaction; b) the diffusion fuel rapidly reacts in the high-temperature zone of the initial flame, increasing its maximum temperature in comparison with that temperature which the pure oxidizer gives.

From equation (3.53) it is evident that dilution can be taken into account by decreasing σ_g . Then the total pressure of the gas in the reaction zone can be expressed from the law of ideal gases as

$$p = p_0 + p_b = (2c_{g,a} + c_{g,b}) R_g T_g, \quad (3.59)$$

where p_0 and p_b - partial pressures of gases of the oxidizer (i.e., NH_3 and HNO_3) and fuel; $c_{g,0}$ - molecular concentration of one of the products of dissociation of the oxidizer; $c_{g,b}$ - fuel.

Solving equation (3.59) relative to $c_{g,0}$ and substituting the obtained solution into equation (3.53), we obtain

$$\gamma = \frac{2R_g T_g}{k_g p (1-L)}, \quad (3.60)$$

where $L = p_b/p$.

Using equations (3.51) and (3.52) and the law of ideal gases, we obtain

$$\sqrt{uk\tau} = \frac{R_g T_g}{p} \left[\frac{2\pi\sigma}{\epsilon_p k_g (1-L)} \right]^{1/2} \quad (3.61)$$

and

$$\delta = \frac{r_0}{1 + \frac{r_0}{R_g T_g} \left[\frac{2\pi\sigma}{\epsilon_p k_g} \right]^{1/2} p (1-L)^{1/2}} = \frac{r_0}{1 + \phi p (1-L)^{1/2}} \quad (3.62)$$

A comparison of equations (3.54) and (3.62) indicates that the effect of dilution decreases the value ϕ for the oxidizer $(1-L)^{1/2}$ times.

The reaction of the fuel in the initial flame can be taken into account by assuming an increased value of the temperature of the flame on the external boundary of the reaction zone

$$T_1 = T_{f,0} + \epsilon. \quad (3.63)$$

Using equations (3.62) and (3.63), it is possible to rewrite equation (3.56) for the rate of combustion in the form

$$B = \frac{\sigma(T_{f,0} - T_s + \epsilon)(1 + \phi p \sqrt{1-L})}{\rho_s \Delta H r_0} \quad (3.64)$$

From equation (3.64) it is evident that, with the exception of ϵ and L , parameters in the expression for the rate of combustion have the same values as those for the pure oxidizer.

Quantity ϵ , just as L , depends on the rate of the diffusion of the fuel into the reaction zone. If we allow that the maximum of L corresponds to the mass ratio of the oxidizer to the fuel, then it can be indicated that $(1-L)^{1/2} \approx 1$ for a stoichiometric composition. This results from the following considerations.

Let us assume that m_r is the mass ratio of the oxidizer and fuel and M_r the corresponding ratio of molecular weights of products of gasification. Then from the law of an ideal gas it follows that

$$p_0 = \frac{M_r}{m_r} p \quad (3.65)$$

and

$$L = \frac{M_r p_0}{m_r p} \quad (3.66)$$

An estimate of values m_r and M_r gives 4 and 0.4, respectively. Then

$$L \approx 0.1 \frac{p_0}{p} \approx 0.1 \quad \text{and} \quad (1-L)^{1/2} \approx 1.$$

The dependence of ϵ upon the rate of diffusion is rather complex, and an accurate estimate of it is difficult. However, for those powder mixtures for which the interaction of the oxidizer with the fuel greatly affects the rate of combustion, ϵ should be directly proportional to the coefficient of diffusion and inversely proportional to the dimensions of the particles. Inasmuch as the coefficient of diffusion is inversely proportional to the pressure, one should expect that ϵ will decrease with a decrease in pressure.

On the basis of experimental data on combustion (Table 30) and equation (3.64), it is possible to determine the change in ϵ depending on the pressure, dimensions of the particles and the mass ratio of the components. In degrees Kelvin for ammonium nitrate powder

$$\epsilon = \frac{7,30 \cdot 10^3 r_p B}{1 + 22 r_p B} - 670^\circ. \quad (3.67)$$

For perchlorate powders

$$\epsilon = \frac{5,03 \cdot 10^3 r_p B}{1 + 56,7 r_p B} - 300^\circ. \quad (3.68)$$

In the derivation of these relations it was proposed that $(1-L)^{1/2} \approx 1$ the change in T_n depending on the rate of combustion was ignored.

Table 30. Data on the rate of combustion.

Fuel	Ratio of masses of the oxidizer and binder	r_p μm	Empirical equation of the rate of combustion (P , at; B , cm/s)
Polystyrene + ammonium nitrate + 3 wt. % $(NH_4)_2Cr_2O_7$	85:15	10	$B = 0,032 + 0,002P$
	80:20	80	$\frac{1}{B} = \frac{3,62}{P} + \frac{4,39}{P^{1/2}}$
Resin on the basis of of styrene + ammonium perchlorate	80:20	8	$\frac{1}{B} = \frac{4,99}{P} + \frac{2,64}{P^{1/2}}$
	75:25	60	$\frac{1}{B} = \frac{6,30}{P} + \frac{6,28}{P^{1/2}}$
	75:25	8	$\frac{1}{B} = \frac{7,19}{P} + \frac{3,39}{P^{1/2}}$

Figure 207 gives the dependence of ϵ upon pressure for the following compositions:

Curves	Oxidizer	Ratio of oxidizer to binder	Mean radius of the particle of the oxidizer, μm
A	NH_4ClO_4	80:20	8
B	NH_4ClO_4	75:25	8
C	NH_4ClO_4	80:20	60
D	NH_4ClO_4	75:25	60
E	NH_4ClO_3	85:15	10

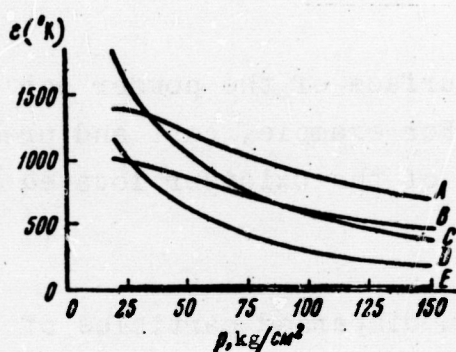


Fig. 207. A change in ϵ with pressure.

Physical role of the binder during the combustion of powders

Powder mixtures are prepared by various means - by polymerization or by casting, including shaping under a vacuum or under pressure, pressing, extrusion and rolling.

The method of the preparation usually governs the final density of the powder, and, as a rule, the greater it is, the more slowly the powder burns. Hence it follows that the basic physical effect of the binder on characteristics of combustion is determined by its effect on the effective surface of the oxidizer, according to which combustion can occur. This follows even from theoretical considerations examined above. The binders which are decomposed at a lower

surface temperature than that of the oxidizer provide the possibility of its combustion on a greater surface, and the combustion in the known degree passes turns into a "volume." The method of the preparation of the powder, the volatility of the binder, and its coupling with the oxidizer can affect the combustion partially also physically.

The same is referred to the ability of a binder to be fused. The binders, which are melted at low temperatures but are rapidly vaporized only at high temperatures, can "fill" the burning surface leading to a temporary extinguishment of the combustions of the oxidizer.

The structure and nature of the surface of the powder can depend on the method of preparation. For example, cast and pressed powders are tightly arranged particles of the oxidizer located in the continuous mass of the fuel.

Pressed charges, probably, contain dispersed particles of fuel distributed in the continuous medium of the oxidizer. Such powders are usually somewhat distinguished according to characteristics of combustion.

2. Experimental Data on the Combustion of Heterogeneous Systems

In the combustion of heterogeneous mixture, the thermal effect of which is determined by the interaction of its constituents of the components, for example, the mixture of the oxidizer and fuel, the rate of combustion, naturally, can depend on dimensions of their particles, inasmuch as the prerequisite of a reaction is the mixing of reactive substances.

Maximum cases of such a mixture are, on one hand, the molecular mixing of the components, as it is carried out, for example, in

solutions or gas mixtures, and, on the other hand - the system in which the half-space, filled by the fuel, borders with the half-space filled by the oxidizer. The possibility of combustion in these last conditions until recently was known only according to the individual observations.

Thus, Dotrish established that the combustion of ammonites is substantially facilitated if the charge makes contact with the carbon; in experiments of A. P. Glazkova on the combustion of ammonium perchlorate in plexiglass tubes, the propagation of combustion along the surface of the contact of the oxidizer and shell forced a search for other materials for the latter. Contact combustion, apparently, can be caused in definite conditions as a result of the interaction of the concentrated nitric acid with walls of an aluminum apparatus. The potential technical value of contact combustion consists in the fact that it indicates possibility of obtaining compositions which can burn but cannot detonate.

Systematically contact combustion was studied in works of Bakhman, Belyayev and their collaborators [205, 206]. Combustion was carried out in charges consisting of a solid inorganic oxidizer, pressed in the form of a rod or plate into heavy-walled cylindrical or flat shells of plexiglass. In those experiments where as a fuel metal was used, the oxidizer was pressed into a brass shell, and in it a hole was drilled into which the powder of the metal was pressed. In experiments with filled density the powder of the metal was poured into a vessel from tracing paper (d from 4 to 12 mm), which was installed on the center in the brass shell, and the clearance between the tracing paper and the brass shell was filled with the powdery oxidizer. The charge was ignited on the upper end along boundary of the fuel-oxidizer, after a short section of acceleration there was established a constant rate of the combustion, the front of which was moved in the form of a conical indentation downward.

The propagation of the flame along the surface of the contact of solid fuel and oxidizer in these conditions includes the gasification of components under the effect of heat flow from the flame, the mixing (because of the encounter of flows directed at an angle to each other and also because of molecular diffusion), the initial heating of products of the decomposition of basic components, and subsequent combustion. In this case near the tip, apparently, there is combustion of a homogeneous mixture (mixing manages to occur within the limits of the zone of heating), and above diffusion flame is established.



Fig. 208. Dependence of the rate of flame upon the characteristic dimension of the layer of the oxidizer (KClO_4 ; $p_{\text{N}_2} = 10 \text{ atm(gage)}$).

1 - cylindrical shell; 2 - flat vessel; 3 - steel vessel.

The dependence was measured of the rate of propagation upon the characteristic dimension d of the layer of the oxidizer, the pressure under which combustion occurred, relative density of the oxidizer, and also the form of indentation. With an increase in d the rate of propagation u in the case of potassium perchlorate decreases, striving toward a certain limit. This change in the rate is connected with the fact that at small distances between plates of the flames, which propagate along the right and left boundaries of the layer d , affect each other by means of heat exchange. With an increase in the thickness of the layer of the oxidizer, i.e., the distances between the flames, this interaction decreases. If we use barium peroxide as the oxidizer, then there will be formed hard and porous black slag, which impedes the thermal interaction of the flame, and the rate of propagation with an increase in d increases, also striving toward a

constant. The independence of u on d indicates the fact that the rate is determined basically by conditions near the tip of the indentation. Indicating this are also results of experiments on the effect of the thickness of films of a number of plastics which were deposited on the plate of the Plexiglas, which burned in the contact with the potassium perchlorate. A layer of polyethylene (thickness, 0.1 mm) increases the rate by 15-20%, and a layer of polyfluoroethylene (Teflon 4), with a thickness of 0.06 mm, decreases it almost two times. With an increase in the thickness of the film the rate increases smoothly (for polyethylene) or decreases (for Teflon), emerging onto the plateau earlier, the higher the pressure. In the latter case, upon reaching a certain thickness of the layer (the larger, the higher the pressure) combustion ceases.

The propagation of combustion depends on the chemical nature of the oxidizer and fuel. Not all oxidizers are capable of the propagation of combustion. Thus, not one of the nitrates studied [$\text{Pb}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, LiNO_3] sustains combustion (in contact with the Plexiglas, although the thermal effect, calculated for complete conversion, for them is more than that for BaO_2 . The propagation of combustion in contact with KClO_4 ($p \leq 60$ at) was not observed for those fuels (polyethyleneterphthalate, perfol', [Translator's Note: this term was not found and is transliterated], galalith, phenolformaldehyde resin FKPM-15), at the thermal decomposition of which in the presence of oxygen great condensed residue is formed.

During the research on systems in which the fuel is a metal, certain characteristics of the combustion of such systems were established. The ability to burn, unlike that which is observed for organic fuels, monotonically decreases with a decrease in the thermal effect of the interaction, being determined by the heat (for mole of oxygen) of decomposition of the oxidizer. In experiments with filled density for aluminum the following sequence (in order of a decrease in q) of these oxidizers was established: KClO_4 , Al_2O_3 , PbO_2 , MKNO_4 , BaO_2 , $\text{Ba}(\text{NO}_3)_2$, MnO_2 , CuO , Co_2O_3 , PbO , Fe_2O_3 , SnO , ZnO , Cr_2O_3 . The last 4 systems did not burn at atmosphere pressure but

acquired this ability at 20 at, with the exception of the system with Cr_2O_3 , which did not burn at a pressure of less than 50 at.

The ability to burn decreases with an increase in relative density of powder of the metal because of too great a heat removal from the zone of reaction. The maximum density increases with an increase in pressure and depends on the diameter of the rod of the metal powder. With an increase in the diameter of the rod, just as for organic fuel, a decrease in the rate of propagation up to some constant is observed. The rate is decreased also with an increase in density of the metal powder, and up, also decreasing, strives toward a certain constant limit; it does not depend (at low rates of combustion) upon the dimension of the particles. Both these characteristics were observed for relatively low-melting metal (Al) and are explained by the formation on the surface of the rod of a layer of melt.

The dependence of the rate of propagation upon pressure for systems Al-KMnO_4 and $\text{Al-Ba(NO}_3)_2$ was linear; for the system W-KMnO_4 the rate of combustion up to a pressure of ~10 at rapidly increases, and from 10 to 60 at it remains constant.

The magnitude of the rate and a form of dependence $u(p)$ for different oxidizers are different (Fig. 209); it is distinguished also for different fuels (with the given oxidizer - KClO_4).

With a decrease in the relative density for the potassium perchlorate at high pressures u increases, apparently, because convection heat transfer from the products of combustion which penetrate the depth of the oxidizer starts to play a role. For barium peroxide and potassium permanganate experiments were conducted only with the small density of the oxidizer, since at large ρ combustion was not propagated.

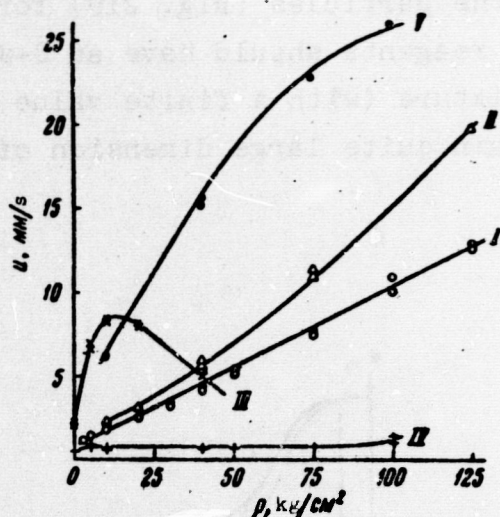


Fig. 209. Dependence $u(p)$ for various oxidizers in a cylindrical shell ($d = 6$ mm) of Plexiglas. I — KClO_4 ($\rho = 0.88$); II — KClO_3 ($\rho = 0.88$); III — BaO_2 ($\rho = 0.35$); IV — KMnO_4 ($\rho = 0.55$); V — the stoichiometric mixture of Plexiglas with KClO_4 (dimension of particles, ~ 10 μm).

With a decrease in dimensions of particles the rate of combustion increases; however, if both components are volatile, this increase is small, and with the increase in pressure the ratio of rates $u_{\text{H}}/u_{\text{H}}$ decreases. For the mixture KClO_4 -Plexiglas this ratio is indicated on Fig. 209 (curve V); u_{H} with the dimension of particles of perchlorate ≤ 10 μm is a total of ~ 3 times more u_{H} .

The increase in the rate of combustion with the decrease in the dimension of the particles will occur only until the width of the zone of mixing of the vapors of the reagents ($\sim u_{\text{nap}} \alpha^2/D$) becomes less than the width of the zone of initial heating ($l_{\text{np}} \sim \lambda/c\rho u \sim \sim 1/p^n$), which corresponds to the homogeneous mixture of the vapors. Hence it follows that the minimum dimension of the particles, below which the rate of combustion stops depending upon it, decreases with an increase in pressure.

Thus, the curve of the dependence of the rate of combustion upon the dimension of the particles (Fig. 210) for systems with a continuous boundary or reagents should have an S-shaped form and for the usual disordered mixture (with a finite value of the diameter) should break at a certain quite large dimension of the particles.

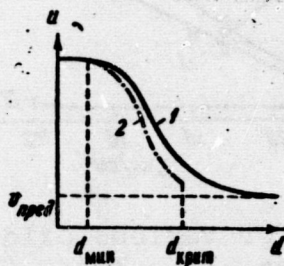


Fig. 210. Asymptotic form of the dependence of the rate of flame upon the dimension of the particles. 1 - ordered mixture; 2 - disordered mixture.

Dimensions: пред = limiting, мин = minimum, and крит = critical.

This conclusion was made during the research on combustion of a stoichiometric mixture of potassium perchlorate with bitumen¹ [207]. The determining parameter here is the dimension of the particles of perchlorate, which are more difficult to gasify, than is bitumen. Figure 211 shows the dependence $u(p)$ for mixtures with a different dimension of particles of perchlorate. This dependence has the form of a palm branch, i.e., the relative increase in the rate of combustion with pressure is more than that for finely dispersed perchlorate.

¹A comparison of the mixture of the type of sulfur-free powder (15% carbon, 85% KNO_3) indicated that it is similar to a perchlorate-bitumen mixture with respect to the weak effect of dimensions of the particles with a dimension of 400 μm to particles of 10-20 μm the rate of combustion at 1-51 at decreases only two times.

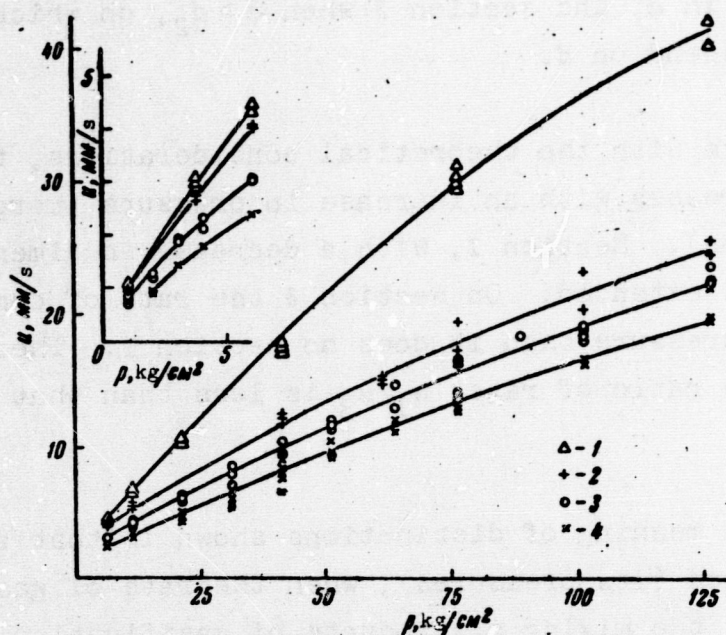


Fig. 211. Dependence of the rate of combustion upon pressure with different dimension of particles of the oxidizer for a stoichiometric mixture KClO_4 with bitumen: 1 - $d = 0.01$ mm; 2 - $d = 0.07$; 3 - 0.2; 4 - 1.7 mm.

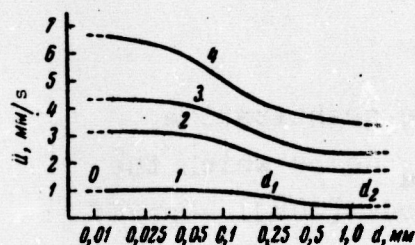


Fig. 212. Dependence of the rate of combustion upon the dimension of the particles of the oxidizer for a stoichiometric mixture KClO_4 with bitumen at various

pressures (in kg/cm^2): 1 - $p = 1$; 2 - $p = 3$; 3 - $p = 5$; 4 - $p = 10$.

In coordinates $u-d$ results of the experiments are given on Fig. 212. Each curve can be schematically represented as the totality of three sections: section 1 from 0 to d , on which the rate does

not depend on d ; section 2 from d_1 to d_2 , on which the rate decreases with an increase in d , and section 3 when $d > d_2$, on which the rate again does not depend on d .

In accordance with the theoretical considerations, the extension of section 1 decreases with an increase in pressure (more accurate, rate of combustion). Section 1, with a decrease in dimensions of the particles, is extended. On section 3 the rate of combustion depends less on pressure than it does on section 1. Therefore, at low pressures the ratio of rates u_1/u_3 is less than that at high pressures.

The physical meaning of distinctions shown is that at the low rates of combustion (low pressures), when the rate of gas-phase reactions is low, the mixing of products of gasification of individual components manages to occur (even in the presence of heavy particles) earlier than the mixture of substances is heated to the temperature of the rapid reaction. Therefore, in entering into the reaction, the gases no longer "remember" what were the dimensions of the particles of those solid components from which they were formed. At high rates of the combustion the rate of chemical conversion is limited by the necessity of the mixing of initial products of gasification, the duration of which is more when the particles were larger (section 2).

Being of interest is the possibility of the quantitative estimate of that dimension of the particles d_{min} below which the combustion of the mixture occurs in a dynamic mode [208]. One of the conditions of the realization of this mode is that the mutual dissolubility of the components at temperatures existing in the preparatory zone of temperatures should be sufficiently great, and the second condition is the quite high rate of mutual diffusion of components in that state into which they pass in the preparatory zone.

Each of the two solid components in the preparatory zone can either remain in a solid state, be melted, or be gasified. Of the six possible variants complete mixing is knowingly possible in the case of the gasification of both components, and practically excluded if one of components is gasified and the other remains in a solid state or passes into a liquid state.

In comparing the rate of the movement of the boundary of the zone of mixing and the zone of initial heating, it is possible to show that $d_{\text{МНН}}$ in the order of magnitude for the case when both components are turned into gases is equal to

$$d_{\text{МНН}} \sim \frac{1}{u_{\text{М}}} \sqrt{\frac{\lambda}{c} \rho_0 D_0} \sqrt{\frac{T_m - T_1}{T_0} + \ln \frac{T_m - T_0}{T_1 - T_0}}, \quad (3.69)$$

where $u_{\text{М}}$ - mass rate of combustion when $d \leq d_{\text{МНН}}$ (in g/cm²s); λ - thermal conductivity (in cal/cm·s·deg); c - heat capacity in cal/g·deg); for both of these magnitudes mean values with respect to the preparatory zone are taken; D - coefficient of diffusion (in cm²/s); T_0 and T_m - initial and final temperatures of combustion; T_1 - lower temperature limit of zone of mixing.

The value of the factor $\sqrt{\frac{\lambda}{c} \rho_0 D_0}$ for all gases which can be products of the gasification of various condensed mixtures is changed within relative narrow limits. Furthermore, if we do not consider the dependence $u_{\text{М}}(p, T)$, which is assigned from an experiment, then the right-hand side of equation (3.69) does not depend on pressure and comparatively weakly depends on the selection within judicious boundaries of T_m , T_1 and T_0 . Having accepted, for example, that temperatures T_m and T_1 can be changed independently in the interval of 1500-3000°K and 600-1000°K, from an expression (3.69) we obtain the following interval of values:

$$d_{\text{МНН}} \sim \frac{1.5 - 35}{u_{\text{М}}} \mu\text{m}. \quad (3.70)$$

Data for the mixture of the potassium perchlorate with bitumen indicate that when $u_M = 0.2 \text{ g/cm}^2\text{s}$ d_{min} is about $70 \text{ }\mu\text{m}$, which agrees with an equation (3.70).

The variant of the realization of the kinetic mode is also the case when the reaction occurs on the surface of particles of one component, but the rate of the feed of the second does not limit the rate of the total process. For this it is necessary that degree of heterogeneity and T_m would not be too great in order that $D_1 \ll D_2$, where D_1 and D_2 - respectively, coefficients of diffusion on the first (forming the particle) and second component into products of reaction. In this case for the solid-gas system the rate of combustion depends on the dimension of the particles ($u \sim d^{-1/3}$), and, consequently, the heterogeneous system is not equivalent to the homogeneous.

In a known degree those prerequisites are satisfied by mixtures of potassium perchlorate with tungsten and graphite, the combustion of which was studied by Belyayev and Tsyganov [209]. In these mixtures only the oxidizer can be decomposed with the formation of the gas phase (oxygen), and the fuels at the temperature of combustion have negligible vapor pressure. It is natural to imagine the process of combustion under these conditions as the reaction of the melted oxidizer or gaseous oxygen on the surface of the fuel.

The rate of combustion of condensed charges depending on the pressure, the ratio of the components and the magnitude of the particles was determined. Mixtures with the graphite of a stoichiometric composition (15% graphite) burn with difficulty in contrast to mixtures with tungsten, which burn by one order faster, are easily ignited, and both with an excess and deficiency of fuel burn stably.

The dependence of $u(p)$ with the change in pressure from 5 to 100 at for the majority of the studied mixtures is similar and considerable;

for mixtures of both fuels not too far from stoichiometric, it is expressed by the power law $u = b p^v$, and values of constants b and v (being changed within limits of 0.3-0.7) complexly depend on the relationship between the fuel and oxidizer, the dimension of the particles of fuel and others.

The effect of the dimension of particles of fuel allow estimating the results of experiments with the mixtures of perchlorate and of graphite (70:30), in which the dimension of the particles of graphite was distinguished by 50-100 times; the rate of combustion with small particles was more than 10 times. Thus, in the examined case the dependence of $u(d)$ is greater than that in systems in which not only the oxidizer but also the fuel are able to be gasified: in the mixture $KClO_4$ -Plexiglas the rate of combustion with a decrease in the dimension of particles of 100 times was increased only 1.5-2 times.

The ratio of the components has a great and unique effect on the rate of combustion. In Fig. 213, plotted along the axis of abscissae is α - the oxygen coefficient of the mixture, and along the axis of the ordinates - the ratio of the rate of combustion at given α to the rate of combustion when $\alpha = 1$. Curve 1 indicates the effect of the ratio of components on the rate of combustion of the mixture with the gasifying fuel - dextrin, curve 2 - to the mixture with graphite (with small dimensions of the particles) and curve 3 - to the mixture with tungsten. For both latter mixtures with an increase in fuel content the rate of combustion increases up to its very large contents - for tungsten, for example, up to 97%. A mixture of 95% W and 5% $KClO_4$ ($\alpha = 0.14$; $T_f \sim 2000^\circ K$) burns at the rate of 20 cm/s. For a mixture with heavy particles of graphite (not given on the graph) the dependence of $u(\alpha)$ is close to that for a tungsten mixture.

The authors explain the obtained results in the following manner. A reaction occurs on the surface of the fuel particles, and its rate w is proportional to the specific surface S . This surface and, consequently, w , is proportional to $1/d$. Inasmuch as $u \sim w$, then $u \sim d^{-0.5}$ in accordance with results of the experiments.

The dependence of the rate of combustion on pressure can be explained by the fact that the rate of the reaction is connected with the concentration of oxygen near the surface of the particles, which is proportional to pressure, or with the quantity of oxygen adsorbed on this surface. Under these assumptions $w \sim p$ (or with absorption it is somewhat weaker than proportional); since $u \sim w^{0.5}$, then $u \sim p^{0.5}$ or somewhat weaker.

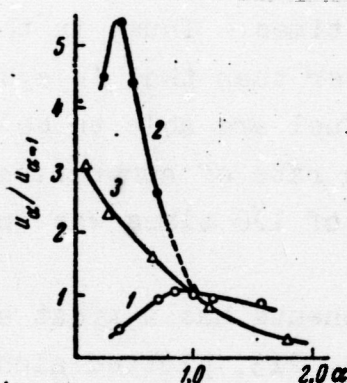


Fig. 213. Dependence $u_\alpha/u_{\alpha=1}$ upon α .

The great increase in the rate with a great excess in tungsten can be conditioned by the great increase in thermal conductivity of the condensed phase; the rate of combustion $w \sim \lambda^{0.5}$. Furthermore, with dilution by the fuel the specific surface increases.

Bakhman and Kondrashkov [210] also examined the case of the combustion of the triple mixture consisting of two gasifying components (for example, $KClO_4$ + bitumen) and a third high-calorific nonvolatile component, for example, tungsten. There was established the effect of the dimension of the particles of this component, which was characterized by the ratio u/u_0 of the rate of combustion in the presence of a third component to the rate of combustion in its absence.

At sufficiently larger dimensions of the particles $u/u_0 \rightarrow 1$ because heavy particles can be ignited and burn down only far beyond the front of combustion of products of gasification of KClO_4 and bitumen, and they will not transfer to the initial substance any considerable part of the energy of combustion. Because of the large dimensions of the particles, the heat consumption for their initial heating and phase conversions up to the termination of the interaction of "volatile" components will also be small. Ultimately the rate of combustion will correspond to the rate of the volume heat release during the interaction of products of gasification of KClO_4 and bitumen (Φ_1 cal/cm³s) at a somewhat reduced temperature in comparison with that of the binary mixture.

An experiment confirmed this conclusion: for the mixture of KClO_4 ($d \sim 10 \mu\text{m}$) with bitumen ($\alpha_0 = 0.75$) with the addition of 13.1% aluminum in the form of large (190 μm) particles u/u_0 at 1 at it was equivalent to 0.99, at 10 at -0.94 and at 100 at -0.96 . If the particles of addition are very small, so that they will be ignited and burn between the surface of the condensed phase and front of the combustion of the binary mixture, then the interaction of the components will occur in two spatially divided stages: in the beginning particles react with products of the gasification of KClO_4 , and then there is a reaction between products of the gasification of bitumen and the remaining part of the products of gasification of KClO_4 . This reaction, as before, remains as the leading one but it occurs now already at another higher (because of the combustion of particles of the third component) temperature and with a different composition of the gas (impoverished by the oxidizer).

With the medium size of the particles, when the zone of the combustion of products of gasification and the zone of the combustion of particles are not spatially divided, the rate of combustion will depend both upon Φ_1 , and upon Φ_2 , where Φ_2 is the rate of volume heat release because of the combustion of the particles. If the lowering of the temperature of gases because of the heat emission

by the particles prevails over the increase in temperature because of the combustion of particles¹ and the total rate of heat release will be less than that in the absence of the particles, then u/u_0 can become less than unity. Curve u/u_0-d will have the form shown on Fig. 214. The presence of a minimum on curve u/u_0-d was verified indirectly: with a constant dimension of the particles the pressure of the experiment was increased; u/u_0 in this case was decreased, apparently, for the reason that particles became "larger" with respect to the thickness of the zone of the combustion of the binary mixture.

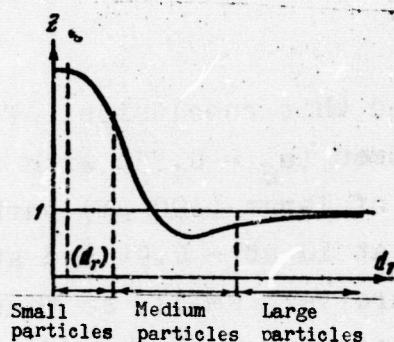


Fig. 214. Effect of the dimension of particles of a nonvolatile component on the rate of combustion of the mixtures with gasifying oxidizer and fuel (Z - ratio of the rate of combustion of a triple mixture to the rate of the binary mixture).

By examining the dependence of the rate of combustion of the binary mixture of the gasifying components upon the dimension of the particles, we saw (see Fig. 212) that in a certain interval of small dimensions the rate is constant, and with a further increase in dimensions of particles it decreases, and then it again becomes constant. This constancy, is apparently conditioned by the fact that the leading stage of the process becomes a contact propagation

¹Binary mixtures of the oxidizer ($KClO_4$) and metals burn considerably more slowly than do the corresponding binary (oxidizer + bitumen) or triple (oxidizer + bitumen + metal) mixtures; this indicates that ϕ_2 is small in comparison with ϕ_1 .

of combustion. However, the independence of u of d can be associated with another side of the phenomenon, namely, with the fact that with sufficiently larger dimensions of the particles (several hundreds of microns and above), besides molecular diffusion, convective mixing starts to play a substantial role; in this case coefficients of mass and heat exchange increase with an increase in d . [211].

The appearance of turbulence is connected with the fact that the initial condensed mixture with disordered arrangement and form of the particles is its kind of "frozen" turbulence, which "activates" with the gasification of the components. The level of such a turbulence is high near the surface of the condensed phase, i.e., in that zone which usually has the greatest effect on the rate of combustion. The basic scale of the turbulence in this case should be proportional to d . Reasons which can lead to the mutual implantation of volumes filled with products of gasification of the components are, first of all, the nonparallelism of flows of products of gasification and the inequality of their absolute rates. The surface of the condensed phase during combustion is not a plane - along the boundaries of the contact of components there are formed the wedge-shaped indentations, which increase with an increase in d . In the immediate proximity to the surface of the condensed phase products of gasification move at right angles to it; therefore, the direction of the motion of gas on the surface is changed from spot to spot and the collision of the gas flows occurs, leading to their mixing.

From the condition of the preservation of the flow of the mass for each of the components $v = \rho u / \rho_n$, where ρ and ρ_n are the density of the condensed component and products of its gasification, and u is the rate of the gasification. Values u_1 and u_2 averaged in time are proportional, but their current values at any moment of time can be found in an arbitrary respect; the densities before and after gasification also, generally speaking, are not equal. Therefore, $v_1 \neq v_2$.

The inequality of absolute magnitudes of rates of products of gasification further their mixing in a tangential ($\perp u_H$) direction and makes convective mixing in axial ($\parallel u_H$) direction possible. When at the given spot of the surface one component during combustion is alternated by the other, along the flow, inasmuch as $v_1 \neq v_2$, there should be either an elementary shock wave (if the rate became more) or the elementary wave of rarefaction (if the rate became less), which, in reflecting from heterogeneities of the density, which exist in the flow, and from the surface of the condensed phase, will generate gradually damping secondary, tertiary, etc., waves. As a result, the flow of the more rapidly flowing gas will be inculcated into the volume of another gas, and the boundary between them will be eroded by the fluctuations in pressure and the rate of the gas, which appear in the passage of elementary waves. The mixing of the gas in an axial direction plays an insignificant role in comparison with the mixing in a tangential direction, since with the gasification of a small cube of the solid component we obtain a rectangular volume of the gas whose dimensions of the base did not change, and the height (and path of mixing) in an axial direction was increased ρ/ρ_r times, i.e., one-three orders.

For the examined turbulence from a parameter with a dimensionality of length (d) and parameter with a dimensionality of the rate ($v_1 - v_2$), it is possible to form a combination having the dimensionality of the coefficient of turbulent exchange (in cm^2/s):

$$D_{\text{тпс}} \sim d(v_1 - v_2), \quad (3.71)$$

in this case for mixing in a tangential direction one should take $(v_{1t} - v_{2t})$ and for mixing in an axial direction, $(v_{1a} - v_{2a})$. Taking into account that $\bar{u}_1 \sim \bar{u}_2 \sim u_H$, we obtain

$$D_{\text{тпс}} \sim du_H \frac{\rho_r}{\rho} \sim \frac{du_H}{p}. \quad (3.72)$$

The coefficient of molecular diffusion $D_{\text{mol}} \sim 1/p$ does not depend on d , and u_{H} is usually proportional to $p^{0.5-0.7}$. Hence it follows that the role of convective mixing increases as d and p increases. It should increase also with the bending of the surface of the condensed phase, inasmuch as in this case the angle of the collision of the streams increases, and inasmuch as the path of mixing in a tangential direction is much less than that in an axial.

For a qualitative check of the role of convective mixing, the height h of the center of the flare was determined during the combustion ($p = 1$ at, $t = 20^\circ$) of cylindrical charges of a mixture of potassium perchlorate with different dimensions of particles (10, 80, and 700 μm) with bitumen. This height not only did not increase, but, on the contrary, it somewhat decreased during the transition from particles with a dimension of 10 μm to 700 μm , which speaks in favor of the increase in the coefficient of mass transfer with an increase in d .

Determination of the height of the flare during contact combustion of the powdery potassium perchlorate, pressed into thick cylindrical snells of Plexiglas with different internal diameter (from 0.4 to 1.4 cm) indicated that $h \sim d$, which should be true with turbulent mixing, while for molecular mixing the relation $h \sim d^2$ should be fulfilled.

The combustion of binary mixtures of potassium perchlorate with aluminum (60:40) was studied [212] also. The mixture was placed into a channel ($d = 9.5$ mm) with polished walls, which was drilled in a Plexiglas rod. Triggering was carried out by a charge of tetryl (0.36 g), exploded with the help of an electric detonator fixed in the opening of the channel. Profiles of the zone of reaction on photographs can be divided into three types; one of them is a cloud with a glowing central region; the other two are distinguished by the fact that they have an extended highly glowing zone, which is

propagated into the depth of the charge; in the case of the third type it is preceded by a forewave — a relatively weakly flowing zone, which retains the constant extension during the whole process;¹ it is probably available with the second type, but the light emission is too weak to be recorded. A photograph on movie film indicates that behind the zone of light emission there follows a dark zone, after which a long "smeared" burning is observed.

The rates of propagation are constant; however, with the ratio of components in the mixture at 60:40 sometimes a sharp increase in the rate — approximately two times (from 480-590 to 810-910 m/s) was observed. A low rate corresponds to the process of the first type, and high rate — one of the two remaining; respectively a change to a big rate, apparently, is associated with the formation of a forewave.

Dimensions of particles of perchlorate weakly affect the phenomenon, and dimensions of particles of aluminum, especially during the transition from small to large, lead to the decrease in the rate of combustion; this indicates the fact that combustion occurs on the surface of particles of aluminum. The presence of a dark zone is supposedly associated with the formation of gaseous Al_2O and Al and the postwave — with the formation of solid Al_2O_3 , when the temperature falls below the critical.

¹The assumption that this zone is a forewave zone is confirmed by the great intensification of light emission with the encounter of zones obtained with the blasting of a charge on both ends. Furthermore, X-ray photographs also indicated the formation and propagation of the zone of increased density. Light emission in this zone can be associated with the initial heating of gas inclusions or with the local chemical reaction.

VII. Burnout of Explosives During Explosive Operations In Mines

During explosive operations in mines, sometimes instead of the explosion of a charge its burnout is observed. This is a very undesirable phenomenon for many reasons. With the burnout [VV] (BB) explosive does not accomplish that action which it should carry out, and toxic gases (NO and CO), which poison the air of the mine are formed in increased quantities. A combustion after a considerable interval of time can turn into an explosion, which kills the blaster who returned to the blast. However, the most serious consequences can be burning in the mines, dangerous in gas or dust, causing ignition of methane or air-dust mixtures.

The possible reasons for burnout and factors favorable to it are diverse. A substantial role in the appearance of burnout is played the ability of explosive to burn, which was studied in a number of works by means of the determination of its various indices - critical diameter, critical pressure and critical temperature.

The critical diameter of combustion and its dependence on density for a number of powdery industrial explosives on the basis of ammonium nitrate were determined [194]. An explosive was put in a conical cellophane or glass case, placed into water, and ignited on the wide end in a bomb of constant pressure. Combustion was conducted at an initial pressure of 100 at, which was raised toward the end of the experiment to 120 at. Results of experiments (Fig. 215) indicate that the critical diameter of studied substances is relatively great and lies between 6 and 13 mm, i.e., considerably more than that for trotyl, which is relatively scarcely able to burn (d_{kr} at 1 at is 21 mm, at 100 at - 1 mm).

The content in ammonite of liquid nitroesters increases the ability to burn. The critical diameter of all the studied explosives (with the exception of Pobedit [PU2] (ПУ2)) is noticeably decreased with the increase in cubic density. Such an effect is somewhat unexpected, inasmuch as the rate of combustion with the increase in

density for all, without exception, studied ammonites, decreases, and more quickly it would follow to expect a corresponding increase in critical diameter.

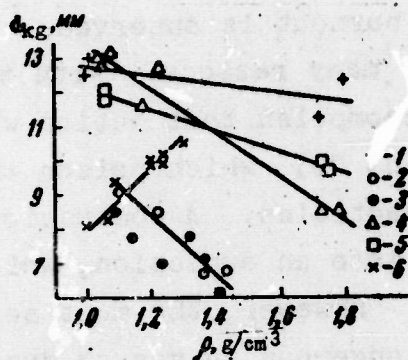


Fig. 215. Dependence of critical diameter of the combustion of certain safety explosives upon cubic density at 100-110 at. 1 - rock ammonite AP-1; 2 - Pobedit VP-1 in a cellophane shell; 3 - Pobedit VP-1 in a glass shell; 4 - waterproof ammonite PJV-20; 5 - ammonite No. 8; 6 - Pobedit PU-2.

The low capacity of ammonites to burn, apparently, is determined by the large content in them of ammonium nitrate the capacity of which to burn is very low. Catalytic agents, however, greatly increase this capacity both in the saltpeter itself, and in an explosive with it as a base. Thus, saltpeter containing 7% common salt burns at 12 at and at a diameter of a charge equal to a total of 7 mm, while the saltpeter itself in similar conditions does not burn even at a diameter of 35 mm and pressure of 1000 at.

The catalytic action of various mineral substances on the combustion of ammonium nitrate was studied by Glazkova [213]. In a manometric bomb the combustion of the pressed charges, which contained 10% of admixture at a density of the charge 0.2 g/cm^3 , was examined. A deficiency of the method is the fact that combustion occurs degressively, and is difficult to determine accurately the end of it, especially as the pressure was measured by a small copper crusher gauge cylinder and the drop in pressure with cooling was not observed. Used as an igniter was black powder in a quantity, which gave with combustion a maximum pressure of 135 at. The indicator of the

catalytic efficiency of the admixture was the ratio of the average mass rate of combustion in its presence to the rate of combustion of saltpeter without an admixture. Appropriate data are given in Table 31.

Table 31. Effect of mineral additions on the combustion of ammonium nitrate in a manometric bomb.

Admixture	P_{cp} , at	u_m , g/cm ² ·s	u_m , %	Admixture	P_{cp} , at	u_m , g/cm ² ·s	u_m , %
Without admixture	187 } 190	0,52 } 0,53	100	$K_2Cr_2O_7$	368 } 362	1,36 } 1,47	270
NaCl	355 } 358	1,45 } 1,43	270	K_2CrO_4	298 } 292	1,24 } 1,17	220
KCl	378 } 335	1,25 } 1,27	240	BaCl ₂	320 } 322	1,60 } 1,57	290
				CaCO ₃ * SiO ₂ **	Combustion was extinguished		

* $P_{atm} = 154$ at.

** $P_{atm} = 145$ at.

A direct comparison of the combustion of saltpeter with admixtures and without them is impeded by the fact that because of the different time of combustion pressures which, naturally, are considerably lower than those calculated for combustion without heat losses are distinguished also. Nevertheless, the table shows that, with the exception of chalk and silicon dioxide, all the studied admixtures substantially accelerate the combustion of ammonium nitrate; acting most powerful is barium chloride, and following it are potassium bichromate, common salt, potassium chloride and chromate potassium.

In safety ammonites the alkaline chloride content is considerably more, and in this case there appears not only their catalytic but also diluting effect as the inert admixture.

The effect of the content of common salt on the combustion was studied by Glazkova [214] in the example of amatol (80:20) in a manometric bomb. In one series of experiments amatol was used in the form of two charges ($d = 11$ mm, $h = 13-14$ mm, total weight, 4 grams). Ignition was carried out by black powder (1.5 grams), which

developed a pressure of 60 at; in another series one charge with a weight of 4 grams ($d = 13$ mm, $h = 17-18$ mm) and an igniter with a weight of 2.5 grams (pressure at combustion 90 at) were used.

Results of the experiments (Fig. 216) indicate that 1% of salt increases by two times the rate of combustion; with an increase in the content of the catalytic agent up to 6.5% the rate continues to increase; with a large content of salt the rate decreases, and with 33% amatol it does not burn even with an increase in weight of the igniter up to 5 grams. When evaluating these results one should take account that, inasmuch as the total weight of the charge was constant, the quantity of actual explosives with dilution by salt was decreased; correspondingly there was a decrease in pressure, which is developed during combustion. One experiment was conducted with a 9% salt content but with a correspondingly increased charge so that the quantity the amatol itself would be 4 grams; the pressure during this experiment was noticeably more, but the rate of combustion was not increased.

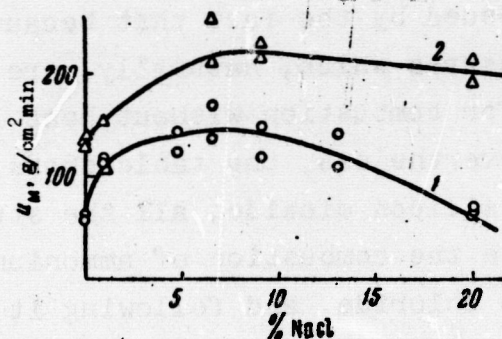


Fig. 216. Effect of the content of NaCl on the rate of combustion of amatol 80:20 in a manometric bomb. 1 - igniter of 1.5 grams of black powder; 2 - 2.5 grams of black powder.

A series of experiments was conducted for a comparison of the effect of various admixtures (9.1%) on the combustion of amatol (80:20) in the form of four-gram charges with the igniter, which gave a pressure of 90 at.

The results of experiments (Table 32) indicate that the most

powerful combustion amatol is accelerated by compounds of hexavalent chromium, especially by potassium chromate; a considerable and approximately identical acceleration is given by chlorides of alkali metals and barium chloride; an oxalic acid ammonium greatly retards the combustion; being less in comparison with potassium chloride, the effect of potassium perchlorate can be connected with the fact that the acting beginning is namely KCl, which with the decomposition of perchlorate is formed two times less than it was added in an experiment with chloride.

Table 32. Effect of mineral additions on the combustion of amatol (80:20).

Admixture	p_{cp} , at	u_m (cp), g/cm ² s	u_m , %	Admixture	p_{cp} , at	u_m (cp), g/cm ² s	u_m , %
Without admixture	251	2,19	100	(NH ₄) ₂ Cr ₂ O ₇	238 } 227 } 281 }	3,35 } 3,88 } 3,85 }	3,69 } 169
LiCl	341 } 194 } 245 }	4,15 } 2,46 } 3,30 }	3,46 } 158	K ₂ C ₂ O ₄	207 } 214 }	3,36 } 3,31 }	
NaCl	258 } 243 }	3,94 } 3,69 }		(NH ₄) ₂ C ₂ O ₄	146 } 196 }	1,06 } 0,91 }	
KCl	301 } 300 }	3,60 } 3,86 }	3,58 } 164	KNO ₃	249 } 255 }	4,18 } 3,34 }	3,76 } 172
BaCl ₂	282 } 264 }	3,29 } 3,98 }		KClO ₄	217 } 256 }	2,94 } 3,45 }	
NH ₄ Cl	245 } 247 }	4,48 } 2,16 }	4,23 } 196	CaF ₂	263 } 267 }	3,07 } 3,84 }	3,34 } 153
HgCl	267 } 263 }	2,58 } 2,24 }		Carbon	258 } 272 }	2,08 } 2,30 }	
K ₂ CrO ₄	213 } 224 }	3,66 } 2,28 }	2,52 } 115	Graphite	273 } 216 }	1,83 } 2,18 }	2,22 } 102
K ₂ Cr ₂ O ₇	222 } 238 }	1,88 } 2,23 }		CaCO ₃	213 } 250 }	2,24 } 3,04 }	
	264 } 261 }	11,89 } 12,66 }	12,19 } 560	SiO ₂	248 } 261 }	2,24 } 3,05 }	2,78 } 127
	268 } 235 }	12,01 } 5,70 }			250 } 215 }	2,69 } 2,43 }	
	237 }	5,40 }			269 } 294 }	2,11 } 2,25 }	

A comparison of data for ammonium nitrate and for amatol indicates that trotyl accelerates the combustion of saltpeter; however, the action of the catalytic admixtures in the latter case has less effect. Thus, common salt accelerates the combustion of saltpeter 2.7 times and that of amatol - only 1.7 times.

Drawing attention is the considerable variance of the given parallel experiments both with respect to p_{makc} , and u , and deviations in these characteristics do not always correspond to each

other in magnitude and even in sign; to a certain extent the variance can be connected with the delay in ignition and with the fact that it occurs not simultaneously at all points of the surface, especially as a relatively weak (90 at) igniter was used. It is possible that this fact is the reason of the considerable divergence in pressures during the combustion of amatol with KCl and NaCl. In spite of the expectation in the latter case, the maximum pressure at 100 at is less.

The catalytic action on the combustion of saltpeter and ammonites is rendered also by that additions of iron salts of organic acids which is introduced for imparting to it of waterproofness. The critical diameter of the combustion of ammonites on iron-accumulating saltpeter containing both common salt and not containing it is twice less, than that in the absence of iron salts. Apparently, iron salts increase the ability to burn only at relatively increased pressures — with a comparison of two Pobedits a great distinction was observed at 100 at and was absent at 18 at. Let us add that the distinction in rates of combustion was very small.

Experiments at low pressures indicated that some catalytic agents, for example, ammonium dichromate, exhibit their effect at atmospheric pressure, and others, for example, potassium chloride, sodium chloride and barium chloride, as was established by A. F. Glazkova, only starting from moderately increased pressures.

During research on the effect of some combined catalytic dopes, which include dichromate and another catalytic agent or a substance which independently does not exhibit a catalytic action, both the intensification and weakening of the effect were observed. If we accept the rate of combustion of the mixture of ammonium nitrate with potassium bichromate ($\rho \sim 1 \text{ g/cm}^3$, $p = 2 \text{ at}$, $d_{\text{TP}} = 16 \text{ mm}$), equal to $0.13 \text{ g/cm}^2 \cdot \text{s}$, for 100, then the replacement of 1/5 dichromate by chloride decreases the rate down to 13, but CaCO_3 , SiO_2 and K_2CO_3 , on the contrary, increase it to 112, 126 and 173, respectively. These three substances by themselves do not give the ammonium nitrate

the ability to burn at low pressures, and the first two even at high pressures decrease this ability.

It is interesting that ignitable substances, as a rule, greatly lower the catalytic action of dichromate, probably, as a result of the reduction of the latter [213].

The effect of catalytic additions, which do not possess an oxidizing function, on the combustion of ammonium nitrate with charcoal is unique. As is known, the addition of carbon greatly increases the ability of ammonium nitrate to burn. A mixture (84.2:15.8) burns at atmospheric pressure with a diameter of 8.5 mm ($\bar{u} \sim 1.5 \text{ g/cm}^2 \cdot \text{s}$); with the admixture of common salt (1-9%) the ability to burn is lost; at 3 at and at an admixture of 1-3% NaCl combustion occurs, but in separate experiments it is extinguished; at an addition of 5 and 6.5% NaCl it occurs stably at a rate considerably exceeding the rate of combustion of a mixture without an addition; with the content of 9% NaCl the rate of combustion of a composition becomes less and again extinguishments are observed; apparently, here the diluting action of NaCl has an effect.

V. G. Khotin determined the critical diameter of the combustion of mixtures of ammonium nitrate with trotyl at atmospheric pressure in glass tubes and in tubes of paper impregnated antipirene (Fig. 217). With the increase in the saltpeter content in the mixture the critical diameter increases and with 50% saltpeter reaches (in glass tubes) 30 mm. Amatol (70:30) did not burn even with the diameter of the glass vessel at 74 mm and with the winding of it with asbestos flex.

With an increase in cubic density the critical diameter of combustion decreases both for trotyl and for amatols (Fig. 218). Experiments at increased pressures were conducted only with amatol (70:30) in order to establish the effect on the critical diameter of some admixtures, which are introduced or can be introduced into the ammonite, primarily sawdust. This addition is introduced for decreasing the condensibility of the explosives, and as was to be expected by analogy with relatively easily ignitable dynammons can increase the ability to burn.

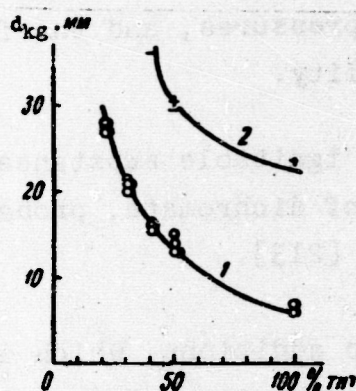


Fig. 217. Effect of the composition of ammonite on the critical diameter of combustion at atmospheric pressure and filled density. 1 - charges in a shell of paper impregnated by a solution antipirenes; 2 - in a shell of glass.

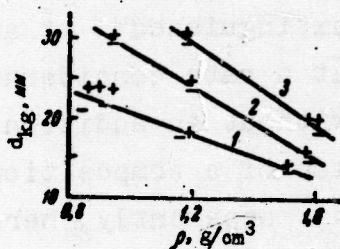


Fig. 218. Effect of density on the critical diameter of combustion of trotyl (1) and ammonites 50:50 (2) and 60:40 (3) in a glass tube.

Results of experiments (Fig. 219) confirmed that sawdust (4%) very greatly lowers the critical diameter at low pressures so that the mixture proves to be able to burn even at 1 at and not too large a diameter (19 mm). However, the dependence of $d_{kp}(p)$ for this mixture is unique. At ~20 at the critical diameter passes through a minimum (8 mm), and then up to 30 at it increases and at 30 at only a little less than that for a mixture without sawdust. Common salt lowers the critical diameter of the amatol, although, apparently, not so greatly as that of the saltpeter itself. Its effect becomes considerable only at pressures above 30 at. At 100 at the introduction of 20% NaCl into the composition of the ammonite, sensitized by PETN, decreased two times the critical diameter of combustion. The addition of nitroglycerine (4%) for the given binary ammonite does not decrease the critical diameter; at 50 at a mixture gives a flash upon ignition.

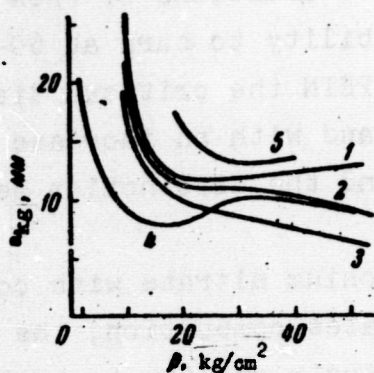


Fig. 219. The effect of certain additions on the critical diameter of the combustion of amatol 70:30 at moderately increased pressures (filled density, glass shell). 1 - amatol 70:30; 2 - amatol 70:30 + 10% NaCl; 3 - 4% trotyl in a composition of amatol 70/30 is replaced by aluminium powder; 4 - 4% trotyl is replaced by sawdust; 5 - 4% trotyl is replaced by nitroglycerine.

It is interesting that the change in the rate of combustion from the presence of addition (Fig. 220) is not in accordance with their effect on the critical diameter: least of all is the rate in the presence of sawdust and aluminum, which most greatly decrease the critical diameter. Connection in the comparison with the possible maximum heat of combustion is not revealed, as the example of the same aluminum or energetically inert common salt, introduced moreover in considerable quantity (10%) indicates.

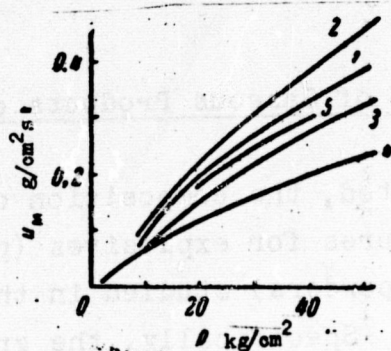


Fig. 220. Effect of certain additions on the dependence of the rate of combustion of amatol 70:30 upon pressure in a glass shell with filled density. 1 - amatol 70:30; 2 - amatol 70:30 + 10% NaCl; 3 - amatol 70:30 in which 4% trotyl is replaced by aluminium powder; 4 - amatol 70:30 in which 4% trotyl is replaced by sawdust; 5 - amatol 70:30 in which 4% trotyl is replaced by nitroglycerine.

The comparative effect of additions of PETN and hexogen (6-10%) to amatol (90:10) on their ability to burn at 60-100 at was studied also. With the addition of PETN the critical diameter is somewhat more with a filled density, and with an increase in the latter the ability to burn increases, and the distinction decreases.

For the mixtures of ammonium nitrate with coal (90:10), which, as is known, greatly facilitates combustion, the effect of the dispersity of components on their ability to burn at atmospheric pressure was studied. The mixture, in which both components were finely pulverized, burns with a diameter (10 mm) approximately two times smaller than that of the other three mixtures (both components or one of them have large particles). Apparently, in the combustion of the given mixture a considerable role is played by reactions which occur at temperatures lower than of the melting point of ammonium nitrate.

Audibert and Del'mas [215] determined the critical initial temperature of combustion at atmospheric pressure of a number of safety explosives used in Franch. Results of these experiments indicate that the rate of combustion was low and was several millimeters per minute. The presence in the composition of the explosives of nitroglycerine promotes combustion. In an even greater degree it is facilitated by the simultaneous presence of sawdust and common salt in chloride grisoudynamite.

VIII. Composition of Gaseous Products of Combustion

As was already indicated, the composition of the gaseous products of combustion at low pressures for explosives (predominantly nitroesters and smokeless powders) studied in this respect does not correspond to equilibrium. Specifically, the greater part of nitrogen is obtained in the form of nitric oxides, while with the establishment of equilibrium practically the entire nitrogen should be obtained in an elementary form.

In experiments of Sarrau and Vieille [216] for nitroglycerine

(in the form of dynamite filler) and pyroxylin during a combustion under a pressure close to atmospheric, has been received the composition of gases given in Table 33. Results of the latest investigations in method described above on methyl nitrate, nitroglycol, weakly gelatinized by nitroglycerine, diglycoldinitrate, pyroxylin, nitroglycerine powder and dynamite are also given in Table 33. From an experiment to experiment the data vary somewhat; here, specifically, the burnout of gases can affect the ignition wire, the completeness of which can be changed.

On the whole, however, distinctions between results of experiments of different authors, which were not produced under strictly identical conditions, indicate relatively small fluctuations. This indicates the fact that reactions of the concluding phase of combustion, which includes the conversion of NO into N_2 , under these conditions of the experiment occur with a comparatively low rate and do not manage to affect noticeably the composition of products of the initial stages of combustion. The stability of the given composition of products of combustion is indicated by the weak effect on this composition of the initial temperature established for certain explosives.

From the data of Table 33 it is evident that during the combustion of nitroesters a great part of the nitrogen and, in certain cases, practically the entire nitrogen, is contained in products of combustion in the form of an oxide.

The great part of the carbon is contained in the form of carbon monoxide. In its basic part hydrogen is oxidized to water. At the same time for some explosives (methyl nitrate, diglycondinitrate and others) the relative quantity of carbon in gases, unlike nitrogen, is considerably less than that in explosives. This indicates that along with carbon-containing gases a certain quantity of carbon compounds being condensed at the usual temperature is obtained; from these compounds for metylintrate, diglycoldinitrate, and at reduced pressures also for nitroglycerine formaldehyde is revealed.

Table 33. Composition of gaseous products of the combustion (without water) of some explosives.

Substance	Content, %							Ratio of the number of atoms of carbon to the number of atoms of nitrogen in		Remarks
	CO ₂	CO	CH ₄	NO	O ₂	H ₂	N ₂	Explosives	Products of combustion	
Methyl nitrate	11.5	33.3	0.4	39.6	0.4	5.5	9.4	1.00	0.77	Average of five experiments
Nitroglycol	8.4	39.6	0.4	45.2	—	4.1	2.4	1.00	0.97	Average of three experiments
Diglycoldinitrate at 18°C	9.4	45.3	2.7	30.1	0.2	10.9	1.5	2.00	1.74	Average of ten experiments
The same at 95°C	9.3	45.7	3.1	29.7	0.1	11.3	0.9	2.00	1.84	Average of three experiments
Diglycoldinitrate gelatinized (97:3) at 18°C	9.7	45.5	3.0	29.4	0.1	10.2	2.0	2.02	1.74	
The same at 95°C	9.9	44.7	3.0	31.1	0.1	9.7	1.6	2.02	1.68	Average of two experiments
Nitroglycerine gelatinized (97:3)	14.0	36.8	0.15	45.4	0.3	1.5	1.8	1.04	1.04	
Nitroglycerine in the form of dynamite filler	12.72	35.86	0.27	48.18	—	1.59	1.29			According to experiments of Sarrau and Vieille
Pyroxylin No. 1	18.3	44.7	1.6	23.9	—	5.3	6.4		1.76	
	19.6	42.2	1.4	24.1	0.2	6.3	6.3	2.18	1.72	Average of three experiments
	18.39	41.94	1.28	24.68	—	7.90	5.81			Average of eight experiments according to data of another work
Nitroglycerine powder with 28% nitroglycerine	16.7	42.3	1.6	28.0	0.4	5.2	6.2	2.35	1.50	According to Sarrau and Vieille
Mixture of ammonium nitrate with coal (84:16)	20.6	5.8	1.4	30.4	0.3	0.2	41.3	0.515	0.246	

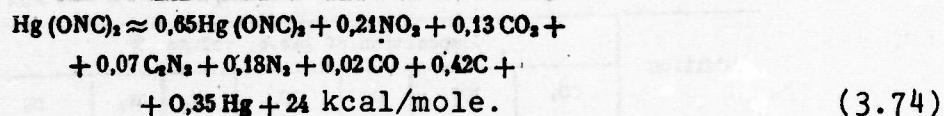
At higher pressures there occurs burnout of products of incomplete combustion, primarily, CO because of the oxygen of NO. For nitroglycol this burnout approaches at pressures between 10 and 14 at and is accompanied by the appearance of a second flame. If at a pressure of 1 at the content of nitric oxides in products of combustion corresponds to 0.9 nitrogen content in explosives and at 9 at - 0.7, then at a pressure of 14-14.5 at the content of the nitric oxide in products of combustion drops to zero.

For other explosives the fact of burnout is also established, but minimal values of corresponding pressures were not determined.

An analysis of the gaseous products of the combustion of mercury fulminate at a pressure of 10 mm, after data of Belyayev, leads to the following equation of reaction:



If one considers that from one mole basic mercury fulminate only 0.35 mole is decomposed, and the remaining part passes the zone of reaction without decomposition and gives a deposit at low pressures, then the summary equation takes the following form:



Thus, the fulminate mercury burns (at low pressures) especially incomplete. This incompleteness is exhibited not only in the composition of the gases, but also in that which the greater part of the substance passes the zone of combustion not having been decomposed, in the form of dust. Correspondingly, the rated temperature of combustion is very low - 750-800°C [217].

The catalyzing additions greatly affect the composition of gaseous products of combustion (at atmospheric pressure) of mixtures on the

basis of ammonium nitrate; primarily this effect is exhibited in the decrease in the content of nitric oxides and in the decrease in the ratio $\Sigma N:\Sigma C$ which approximates it to the rated. This last fact indicates the fact that the oxidation of carbon, which is very incomplete in the absence of addition, increases more greatly than the dissociation of ammonium nitrate (an exception is barium chloride).

Tables 34-36 give appropriate data for a number of mixtures.

Table 34. Effect of catalytic additions (6.5%) on the composition of products of combustion of a mixture of ammonium nitrate-trotyl-coal.*

(Theoretical ration $\Sigma N:\Sigma C$ is equal to 2.4; $\rho = 1.4-1.6 \text{ g/cm}^3$; temperature, 100°C).

Addition	Composition of gases, volume %**							$\Sigma N:\Sigma C$ (experimental)
	CO ₂	NO	O ₂	CO	CH ₄	H ₂	N ₂	
—	14,9	25,8	0,3	12,3	1,3	0,14	48,8	4,5
NaCl	20,4	12,3	0,5	12,6	1,5	2,6	50,1	3,3
KCl	19,1	13,1	0,3	11,6	3,4	6,1	46,2	3,1

*To amatol (80:20) 5% coal was added.

**Average of two experiments.

Table 35. Effect of catalytic additions (6.5%) on the composition of products of combustion of dynammon (84:16).

(Theoretical ratio $\Sigma N:\Sigma C$ is equal to 1.9).

Addition	Composition of gases, volume %							$\Sigma N:\Sigma C$ (experimental)
	CO ₂	NO	O ₂	CO	CH ₄	H ₂	N ₂	
—	20,6	30,4	0,3	5,8	1,4	0,2	41,3	4,1
K ₂ CrO ₄	22,4	0,0	1,2	10,3	1,8	7,8	56,5	3,3
BaCl ₂	17,7	0,1	1,2	8,1	1,7	2,3	68,9	5,0
K ₂ Cr ₂ O ₇	22,2	3,9	0,5	13,6	2,3	10,8	46,8	2,6
NaCl	23,5	8,3	0,6	7,9	1,6	3,2	54,8	3,6
KCl	22,4	24,5	0,5	6,1	1,4	2,8	42,3	3,6
NH ₄ Cl	22,7	26,2	0,6	6,7	0,4	0,1	43,4	3,8

Note: The table gives average values from 2-3 experiments. Combustion was produced in tubes with a diameter of 15 mm.

Table 36. Effect of catalytic addition (6.5%) on the composition of products of combustion of dynammon (84.2:15.8).

(Theoretical ratio $\Sigma N:\Sigma C$ is equal to 1.94; $\rho = 1.3-1.4 \text{ g/cm}^3$, $d = 25.4 \text{ mm}$).

Addition	Composition of gases, volume %							$\Sigma N:\Sigma C$ (experimental)
	CO ₂	NO	O ₂	CO	CH ₄	H ₂	N ₂	
Without admixture	22,4	14,4	0,3	3,9	0,7	1,2	57,1	4,8
	18,5	27,3	0,3	3,5	1,0	1,4	48,0	5,4
	27,6	0,1	1,0	2,4	1,4	2,5	65,1	4,2
BaCl ₂	20,0	0,0	6,0*	1,3	1,3	1,0	70,4	—
KCl	23,2	0,6	2,6	1,6	1,8	1,4	68,9	5,2
	29,0	1,5	0,4	1,5	4,5	2,6	60,5	3,5
NaCl	27,5	7,2	0,5	6,3	0,7	1,0	56,9	3,5
	27,4	3,9	0,1	6,5	1,4	3,2	57,5	3,4

*Increased quantity of oxygen is conditioned, apparently, by nonabsorbing CO₂.

IX. Temperature of Combustion

Any spectroscopic phenomena dependent on the temperature of the gas can be used for its measurement. The spectroscopic methods for the measurement of this temperature are: the method of resonance inversion of spectral lines, accepted both for visible and infrared regions of the spectrum, the method of the distribution of intensity in rotational lines of the band spectrum a dichromatic pyrometric absolute radiation method and the method of Doppler expansion of the spectral lines. The first of these methods consists in the following.

If the radiation of the flame is thermal, i.e., if various states taking part in the process of irradiation are in thermodynamic equilibrium, then the temperature of the flame can be measured by the method of the inversion of spectral lines. With the introduction into the flame, for example, of common salt, with its vaporization and dissociation sodium of atoms can be formed, which can be excited and emit a yellow D-dublet sodium with a wavelength of 5890-5896 Å. If we place behind the flames a black body and direct toward it through the flame the slit of the spectroscope, then at the same temperature

of the black body, the so-called temperature of inversion, its illumination in the spectral region of the D-lines will be equal to the luminosity passing in this region through the flame plus the illumination of D-lines from the very flame. Only at this temperature observable in the spectroscopy will be a continuous spectrum while at any other temperature the lines of sodium will be separated as bright or dark against the background of the continuous spectrum of the black body depending on what the temperature of this body will be above or below the temperature of inversion. If we determine the temperature of inversion and the absorbing power of the flame, then it is possible to calculate its temperature.

The temperature of the flame can be studied by means of comparing the quantity of energy being emitted by the thin metal wire heated by an electrical current and located (in one experiment) in a high vacuum, and in another - in the flame being studied. It is obvious that the wire in the flame emits at a given force of the heating current as much energy as that in a vacuum, only if the temperature of the wire is equal to the temperature of the flame and it does not lose heat because of thermal conductivity but gives up it, just as in a vacuum, only due to radiation. The temperature of the heated wire in a vacuum can be measured by an optical pyrometer.

In principle the methods described and methods similar to them can be used for the determination of the temperature of combustion of explosives; however, appropriate works, especially at low pressures, have not been published.

The optical method of blue-red ratio was used by Mal'tsev and others [218] to obtain the distribution of temperature in the gas phase (from 800°-1000°C and above) during the combustion of ballistite powder under a pressure of 20-70 at. The distribution of temperature on an oscillogram has a step form, which with an increase in pressure approaches toward the surface.

In a number of works for the measurement of the temperature profile of combustion, thermoelectric couples were used.

The distribution of temperature in the zone of combustion is the result of the liberation or absorption of heat by chemical reactions and its transfer from hot layers by colder ones. Therefore, knowledge of the profile of temperature is necessary for the quantitative characteristic of physicochemical processes during combustion.

One of the possibilities of the determination of the indicated profile is the measurement of the change in temperature in the course of combustion with the help of thin low-inertia thermoelectric couples. The detailed development and theoretical basis of this method both for gas and for the condensed part of the zone of combustion are given in the work of Zenin [219].

Thermoelectric couples were used for the given purpose earlier, but the method of their use contained considerable errors revealed in the mentioned work. A certain condition of validity of thermocouples measurements is the use of thermocouples of Π -shaped form.

Zenin examined the heat exchange of the thermocouples with a gas medium, experimentally determined the coefficients of heat transfer of the thermocouples used, calculated the understanding of the temperature being measured by the thermocouple of the most general Π -shaped form because of the thermal inertness of the thermocouple and heat losses into ends of thermocouple by means of thermal conductivity and radiation. The relative error as a result of heat losses into ends of the thermocouple decreases with an increase in the rate of combustion, and it sharply increases with a decrease in the magnitude of the arm; the error because of thermal mass inertia rapidly increases with an increase in the thickness of the thermocouple; thermocouples with a thickness of 7 μm give a quite good recording of the temperature up to the rate of combustion of 0.5-0.8 cm/s.

Experimentally and by calculation it is shown that the thermal inertness of thin thermocouples, coated for the prevention of a catalytic effect by a thin layer molten borax, is equal to the thermal inertness of bare thermocouples of the same thickness.

This is determined by the fact that under the given conditions the rate of the initial heating of thermocouples is so greatly limited by heat supply from the gas phase that even in the poor heat conductors the change in temperature with respect to thickness of the thermocouples is used, i.e., their thermal inertness does not depend on the thermal conductivity of the material.

Similarly, the heat exchange of a thermocouple with a condensed medium was examined. On this basis, together with the estimate of the rigidity of the Π -shaped thermoelectric couple, criteria were developed which parameters of thermocouples should obey in order to provide a reliable recording of the temperature profile. The methods developed were used for research on the combustion of nitroglycerine powder H at various pressures and temperatures. The obtained results allow calculating the quantities of heat which is liberated as a result of chemical reactions in the condensed and gas phases, the feed of heat from the gas phase into the condensed and the effective energy of the activation of decomposition of the condensed phase.

Two methods of the use of a thermocouple for measurement in the gas phase of the distribution of temperature formed during the stable combustion of a condensed explosive are possible. With one of these the position of the thermocouple relative to the zone of combustion is invariable. This condition can be accomplished in two ways - by movement of the thermocouple placed at a certain spot of the temperature distribution at the rate of motion of the flame or by movement of the burning surface relative to the thermocouple at the rate of combustion.

Under these conditions the thermal inertness of the thermocouple has no value, and one should take measures against heat emission into ends of the thermocouples (or an increase in heat from ends on the thermojunction) and select sizes of the thermocouple considerably less than the width of the zone of alternating temperature.

It is difficult to use this method with the small thickness of the region of alternating temperature and high rate of the propagation of combustion. In this case more suitable is the second method - a

thermocouple rests relative to the basic condensed explosive, and the flame passes through it at the rate of the combustion. Besides taking into account heat transfer into ends of the thermocouple and the necessary quite small thickness of the thermocouple, the thermal inertness of the thermocouples should be taken into account and made small.

The distribution of temperature during combustion in a solid can be obtained only by the second method. For a correct measurement of the distribution of temperature, the shape of the thermocouple is of importance. Arrangement on an angle leads to great thermal losses into the ends, and with the arrangement of the thermocouple along the isotherm the rigidity of its attachment is lost; both of these deficiencies are eliminated in a Π -shaped thermocouple.

Calculations conducted for the condensed phase indicated that a relative error due to the thermal inertness of the thermocouple increases in proportion to the thickness of the thermocouple and rate of combustion. For thermoelectric couples with a thickness of 3.5-7 μm it is quite small. Errors due to heat removal into the ends can be decreased by an increase in the magnitude of the arm of the thermocouple. On the whole conditions of a measurement are more difficult in the gas phase, and if they are fulfilled, then measurements in the condensed phase will also be errorless.¹

Zenin measured the distribution of temperature during the combustion of power H. Two groups of band Π -shaped thermocouples were used: 1) copper-Constantan, manganin-Constantan (thickness, 5 and 2 μm), which possess a high thermoelectromotive force and different thermal conductivity but do not allow the measuring of temperature above 1000°C and 2) tungsten +5% rhenium-tungsten +20% rhenium, tungsten-molybdenum +5% aluminum (thickness, 7-3.5 μm); the thermoelectromotive force of these last thermocouples is 4 times less than

¹Estimates are given in reference to the ballistite powder H.

that in thermocouples of copper-Constantan, but, being high-melting, they allow measuring the temperature profile completely up to a maximum temperature in the flame.

Thermocouples were glued in pairs with the help of acetone into longitudinally or transversely cut powder of charges; this made it possible simultaneously with the determination of the temperature profile to measure the rate of combustion in the given experiment.

Curves $t(s)$ for different pressures lower than atmospheric at an initial temperature of the powder of 125°C are given in Fig. 221. In a vacuum the temperature of the gas phase does not increase but fluctuates with an amplitude of $10\text{--}20^{\circ}\text{C}$. With an increase in pressure the maximum temperature increases, and its zone approaches to the surface of the powder. Starting from 200 mm Hg the gas phase starts to affect the rate of combustion by means of heat feed into the condensed phase; starting from 300 mm the feed of heat is possible from the zone of maximum temperature.

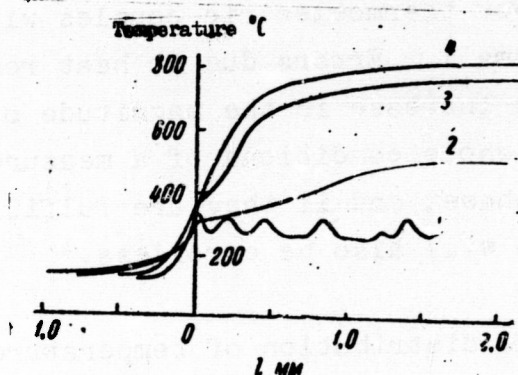


Fig. 221. Temperature profiles during the combustion of powder H in a vacuum at 120°C and different pressure (in mm Hg): 1 - $p = 0$; 2 - $p = 100$; 3 - $p = 300$; 4 - $p = 600$.

The temperature of the surface increases with an increase in the initial temperature of the powder and slightly increases also with pressure.

The heat release in the condensed phase barely depends upon pressure, and the heat release in the gas phase rapidly increases with

an elevation in pressure up to 200 mm when it becomes two times more than the heat release in the condensed phase; with a further increase in pressure up to 600 mm, the heat release increases very slowly. The portion of the increase in heat from the gas is at 200-400 mm about 5% of the total amount of heat of the condensed phase. The rate of combustion depends very slightly upon the temperature of the condensed phase.

The temperature profile was determined by tungsten-rhenium by thermoelectric couples at increased pressures (up to 150 at). Figures 222, 223 and 224 show temperature profiles and heat release at different pressures. Conditionally accepted as the temperature of the surface is that at which temperature the curve changes its form. The heat release was calculated from the equation of thermal conductivity in a stationarily propagating thermal wave with heat release

$$\lambda \frac{d^2T}{dx^2} - \rho u \frac{dT}{dx} + \Phi(x) = 0, \quad (3.75)$$

the first two terms of which were calculated by differentiation of the temperature curve. The first maximum of heat release is, obviously (it was observed even during combustion in a vacuum), heat release in the condensed phase, i.e., it corresponds to that point of it where the temperature is the greatest. Correspondingly, this temperature is assumed to be the temperature of the surface of the condensed phase. Values of this temperature at different pressures are presented in Fig. 225. These temperatures are higher (by $\sim 40^\circ$) than those measured [220] by the thermocouple pressed against the surface of the powder.

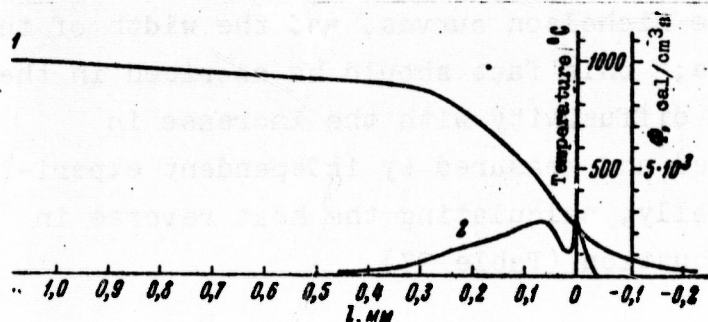


Fig. 222. Temperature profile (1) and rate of an heat release (2) during the combustion of powder H ($p = 5$ at; $u = 1.38$ mm/s).

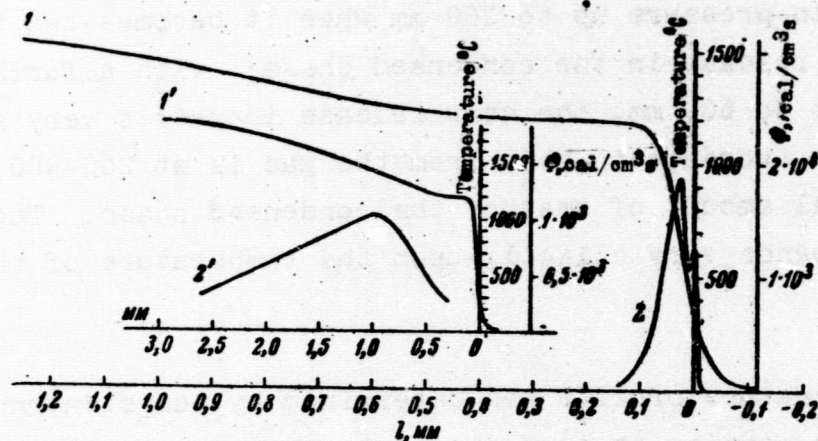


Fig. 223. Temperature profile (1, 1') and the rate of heat release (2, 2') for powder H at 30 at.

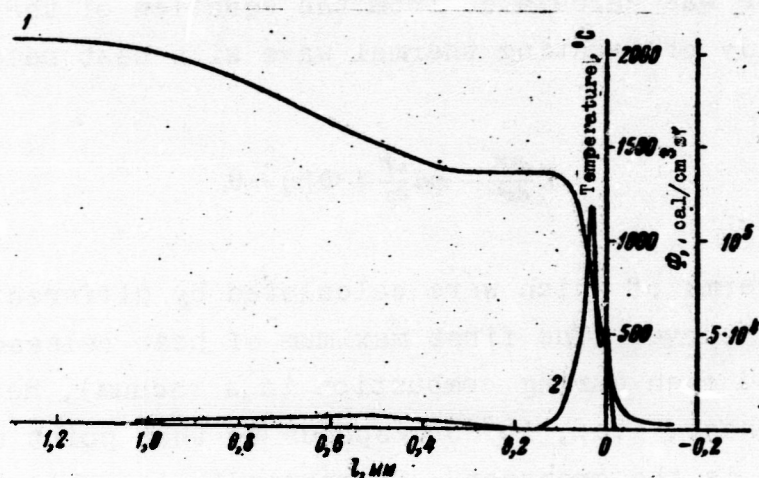


Fig. 224. Temperature profile (1) and the rate of heat release (2) for powder H at 75 at.

Distribution curves of temperature in the condensed phase are somewhat distinguished from the Michelson curves, and the width of the zone of initial heating is more; this fact should be ascribed in the first place to the increase in diffusivity with the increase in temperature, which was confirmed and measured by independent experiments. This allowed, specifically, calculating the heat reverse in heated layer during steady combustion (Table 37).

Table 37. Heat reserve in the condensed phase during steady combustion of powder H at various pressures.

p, at	5	10	20	50	75	100
$Q, \text{cal/cm}^2$	1,0	0,9	0,72	0,50	0,45	0,40

For the distribution of temperature in the gas phase, it is characteristic that it does not at once increase up to the maximum value, which corresponds to complete combustion, but has a step in the region of 1000°C ; at 20 at there appeared the flame with a maximum temperature, which with an increase in pressure approached the surface (Fig. 226), and its temperature increases up to a certain constant (2050°C). The calculated curves of heat release, depending on temperature at 10 and 20 at, are given in Fig. 227. Apparently, they are the consequence of several reactions occurring in parallel and in series, which especially substantially allow for the smoke-gas zone where reactions can occur even in gas and in dispersed particles.

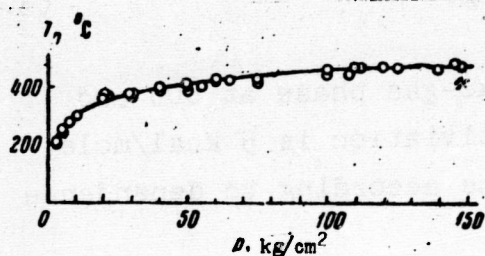


Fig. 225. Temperature of the surface of the burning powder H depending on pressure.

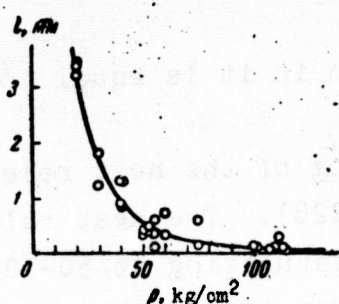


Fig. 226. The change in the distance of the flame upon the surface depending on pressure for powder H.

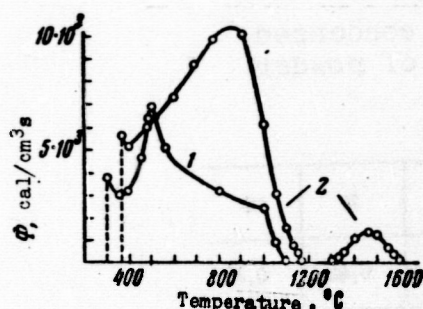


Fig. 227. Rate of heat release in the vaporous smoke-gas zone as a function of temperature during the combustion of powder H 1 - $p = 10 \text{ kg/cm}^2$; 2 - $p = 20 \text{ kg/cm}^2$.

A. A. Zenin also produced calculations of the order of the reaction and its energy of activation for different zones. These calculations are based on the formal assumption that the rate of heat release is proportional to the concentration of reagents to the power equal to the order of the reaction

$$\Phi(T) = A \cdot e^{-E/RT} n_0^v \left(\frac{T_{\text{KOH}} - T}{T_{\text{KOH}} - T_c} \right)^v. \quad (3.76)$$

If we take the value of Φ at a fixed temperature but at various pressures, then along the slope of the straight line

$$\lg \Phi_{\text{KOH}} = B + v \lg p \quad (3.77)$$

It is possible to obtain v . For the smoke-gas phase at 600 and 700°C v is equal 1, and the energy of activation is 5 kcal/mole. For the beginning of the zone of the flame according to dependence

$$\ln \Phi(T) = f\left(\frac{1}{T}\right) \quad (3.78)$$

$E = 50 \text{ kcal/mole}$, and the order of reaction in it is equal to 2.

The obtained data allow the calculating of the heat release in various zones depending on pressure (Fig. 228). The heat release in the condensed phase increases at 5-50 at, saturating at 50-100 at, possibly, in connection with the decrease in dispersion. An increase in the heat release in the smoke-gas and flame zones occurs, apparently, as a result of the increase in the completeness of the

reactions: the total completeness of combustion is reached at about 60 at.

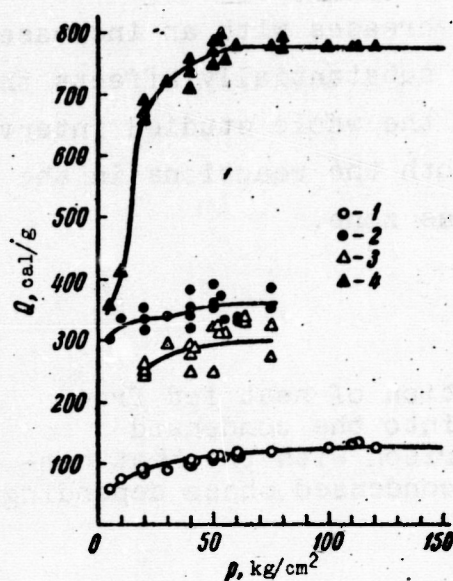


Fig. 228. Quantity of an heat which is liberated as a result of chemical reactions (powder H): 1 - in the condensed phase; 2 - in the vaporous smoke-gas zone; 3 - in the flame of zone; 4 - total heat release during combustion.

It is evident that the dependence $u(p)$ has a complex character: at pressures of 1-4 at the rapid increase in rate is observed, then it is slowed down, and at 4-8 at almost a plateau on the curve of the dependence of the rate of combustion upon pressure is observed. At 8-10 at again the increase in rate is observed, but considerably less. From Fig. 229 it is evident that the further course of the rate of combustion on pressure has no characteristics.

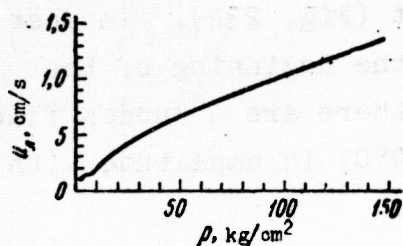


Fig. 229. Dependence of the rate of combustion of powder H upon pressure.

Zenin connects the unique dependence $u(p)$ in the region of pressures up to 10 at with the fact that $E_{\kappa\Phi}$, calculated from the dependence $u(T_{\Pi})$, at low pressures is small (6.5 kcal/mole), and when $p > 10$ at it is considerably more than 26 kcal/mole. On this basis one can assume that the mechanism of decomposition of the condensed phase is different in both regions.

The flow of heat from the gas phase into the condensed phase increases with an increase in pressure as a result of the increase in temperature gradient of the surface. The portion of the heat fed from the gas phase into the condensed phase, in comparison with the heat which is contained in the latter, decreases with an increase in pressure (Fig. 230). Simultaneously, it substantially affects the rate of combustion, and in this sense in the whole studied interval of pressures the leading reactions are both the reactions in the condensed phase and in those the smoke-gas zone.

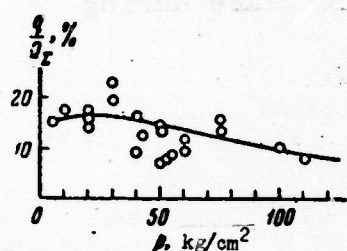


Fig. 230. Portion of heat fed from the gas phase into the condensed phase in comparison with the heat contained in the condensed phase depending on pressure.

The profile temperature during the combustion of greatly pressed ($\rho = 1.93\text{--}1.94 \text{ g/cm}^3$) ammonium perchlorate in charges with a diameter of 7 mm was studied [221] with the help of Π -shaped thermocouples, tungsten-rhenium 5/20, circular ($d = 30$ and $15 \mu\text{m}$) and strip with a thickness of 7 and $3.5 \mu\text{m}$.

In the interval of the pressures of 30-150 at, the recordings have the usual character (Fig. 231). They look completely different in the interval of the pressures of 160-350 at (Fig. 232). In most cases the plateau of temperature is observed in the beginning of the temperature profile ($250\text{--}300^\circ\text{C}$), and then there are a sudden fluctuations of temperatures, which reach 500° ($1000\text{--}500^\circ\text{C}$) in amplitude with a period of $\sim 50 \text{ ms}$.

Photographs of combustion obtained on a photographic recording also have an uncommon form - irregular cessations of combustion and correct alternations of darkenings and light spots on the layer, the average period of which is close to the period of the oscillations in temperature are observed.



Fig. 231. Typical oscillogram of combustion of ammonium perchlorate in a stable region.

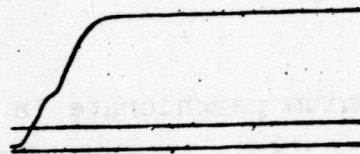


Fig. 232. Oscillogram of the combustion of ammonium perchlorate in an unstable region ($p = 250$ at).

The distribution of the rate of heat release at two pressures is shown on Figs. 233 and 234.

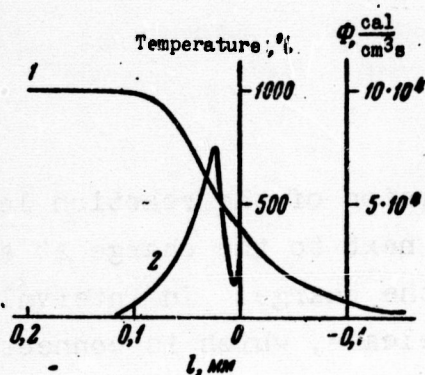


Fig. 233. Temperature profile (1) and the distribution profile of the rate of heat release (2) during the combustion of the ammonium perchlorate ($p = 50$ at).

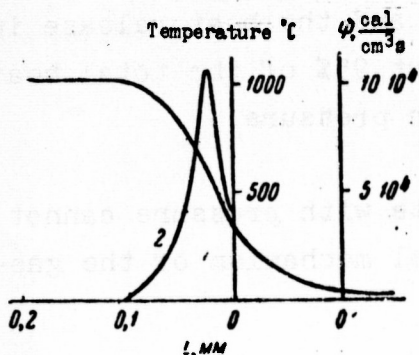


Fig. 234. Profile temperature (1) and distribution of the rate of heat release (2) during the combustion of ammonium perchlorate ($p = 100$ at).

The temperature of the surface in the region of unstable combustion, measured by the thermocouple with small loads, was 270°C in the interval of pressures of 160-350 at. The maximum temperature of combustion passes through a maximum at 150 at (1050°) and decreases at 900°C at 300 at.

The heat balance of the combustion of ammonium perchlorate in its stable region is shown on Fig. 235. Its characteristic is the drop in temperature of the surface with an increase in pressure, especially low in the region of unstable combustion, and the great heat release in the condensed phase.

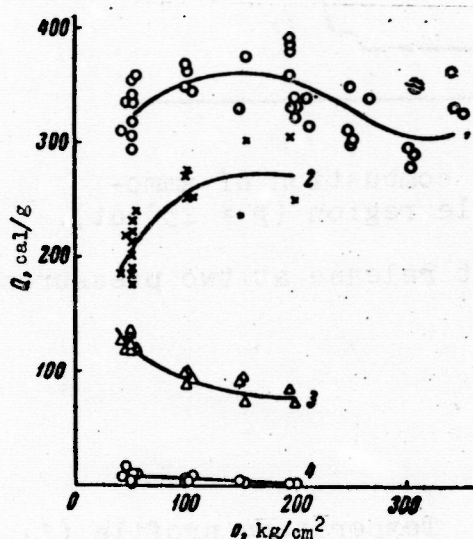


Fig. 235. Dependence of total heat release (1), heat release in the gas (2) and condensed (3) phases, and also heat arrival from the gas phase (4) during the combustion of ammonium perchlorate upon pressure.

Attention is given also to the dispersion of the reaction layer, which can be observed on the glass placed next to the charge at a height exceeding 2-3 times the height of the charge. In interval of 40-150 at an increase in the total heat release, which is connected with its great increase in the smoke-gas phase is observed. However, the feed of heat from the smoke-gas phase into the condensed phase is small and is weakly changed with pressure, and the heat release in the condensed phase, which consists of about 95% of the total heat in the heated layer, drops with an increase in pressure.

Thus, the observed increase in the rate with pressure cannot be explained with the help of the usual thermal mechanism of the gas-phase combustion.

According to the curve of the rate of the heat release in the gas phase, the energy of an activation, calculated from equation

$$u \sim p^{n_2} e^{-E/RT_s}, \quad (3.79)$$

at 30-150 at is 10-12 kcal/mole.

Powling and Smith [222] determined by means of the measurement of radiation at definite wavelengths in the infrared part of the spectrum (3.7 and 7.1 μm) the temperature of the surface during the combustion of the mixtures of ammonium perchlorate with easily gasifying fuel (paraformaldehyde) at the low pressures (25-760 mm). At atmospheric pressure the temperature of the surface does not depend upon the rate of combustion (the latter was changed, specifically, by means of a change in the fuel content). Hence the conclusion was drawn that on the burning surface there is carried out thermodynamic equilibrium between the solid ammonium perchlorate and products of its dissociation - ammonia gas and perchloric acid. With the correctness of this conclusion the temperature of the surface should have depended on pressure, which was confirmed experimentally (Fig. 236).

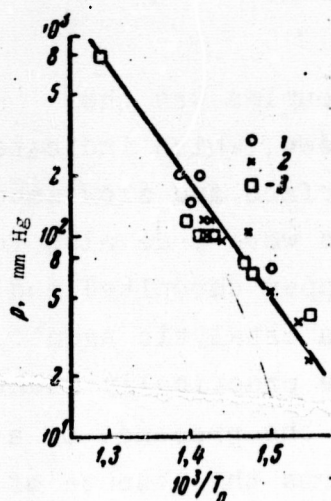


Fig. 236. Dependence of the temperature of the surface on pressure with the combustion of the mixtures of ammonium perchlorate with paraformaldehyde (in %): 1 - 10; 2 - 12.5; 3 - 24.3. The wavelength in the determination of temperature is 7.1 μm .

The temperature of the surface was determined for the mixtures containing 10-24.3% of fuel in the interval of pressures of 760-25 mm. At the given pressure the fuel content weakly affects the temperature of the surface, although the rate of combustion with the change in

fuel content changes greatly. Dependence $\lg p - \frac{1}{T_s}$ is expressed by a straight line, and from the tangent of the angle of inclination the thermal effect of the process is equal to 57 kcal/mole, which practically coincides with the heat of the dissociation of the solid ammonium perchlorate into ammonia and perchloric acid (56 kcal/mole). The application of fuels which are gasified more difficultly than that of paraformaldehyde (for example, polystyrene) gives higher temperatures of the surface, but the inclination of the straight line $\lg p - \frac{1}{T_s}$ is not changed. It is possible that this increase in temperature is conditioned by the fact that on the surface, together with the perchlorate, there are also particles of fuel or products of its decomposition which possess higher temperature. However, high temperatures of the surface were observed only when the fuel is more difficult to be gasified or its content is great. In order to provide the possibility of the combustion of mixture at low pressures, it is necessary to add relatively a large amount of fuel, for example, at 25 mm about 50% of that which is stoichiometrically necessary.

The independence of the rate of combustion of temperature of the surface indicates that the reaction occurring on the surface is an equilibrium and not leading reaction but driven by exothermic gas-phase reactions.

Also measured with the help of thin thermocouples was the distribution of temperature in solid and gas phases, which indicated the change in the temperature gradient on the surface and slow secondary reactions in the gas phase. These determinations were made also for the mixtures containing a catalytic agent (3% copper chronite) and burning two times faster than in the absence of a catalytic agent. The temperatures of the surface were in this case practically identical, and the temperature gradient in the gas phase in the presence of a catalytic agent is more, which furthermore confirms the absence of a leading role of processes which occur on the surface. Agreeing with this also is the fact that the preliminary preheating of ammonium perchlorate to 350°C does not affect the temperature of the surface.

However the described situation is realized only at low pressures;

at increased pressures the zone of high temperature approaches the surface, and the concentration of NH_3 and HClO_4 tends to zero.

It is possible that connected with this is the sudden decrease in the dependence of the rate of combustion upon pressure, which is observed at about 70 at for weak mixtures of fuel with ammonium perchlorate.

An attempt was made [125] to measure the temperature of the combustion of nitroglycol by means of the introduction into the liquids through the bottom of the tube of silver and copper wires with thickness of 0.25 mm with tapered ends. In two experiments the silver wire was fused, but the copper did not. Thus, it appeared possible to conclude that the temperature of combustion of nitroglycol lies above 960° and below 1080°C . However, it was not excluded that initial heating and the fusing of the silver wire are conditioned to a certain extent by the catalytic reaction occurring on its surface of the burnout of intermediate products of combustion. This is indicated, specifically, by the fact that with the ignition of the platinum or nichrome wire the latter frequently continued to glow for a long time after the turning off of the current.

To check this assumption the experiment on nitroglycol was repeated, and in the first place, the temperature of the nitroglycol was above (75°C), and, in the second place, besides silver and copper wires, put into nitroglycol was a platinum wire. It was expected (if the temperature of combustion of the nitroglycol at 20°C lies nearer to 1080° than to 960°) that with the increase in the initial temperature of the nitroglycol by 55° the temperature of combustion will rise respectively, and the copper wire will also be fused. However, as before fusing of the copper wire did not occur. At the same time the platinum wire was fused considerably greater than silver. Thus, with this method of the tentative estimate of the temperature of combustion (and also during the measurement of the temperature of combustion by thermocouples from appropriate metals) only a negative result, i.e., the absence of fusing is reliable. Furthermore, it must be kept in mind that with the described posing of the experiment, the temperature of

the wire, as a result of the good thermal conductivity of the metal, does not reach the temperature of the gases. In order to decrease the effect of thermal conductivity in one of the experiments with nitroglycol a copper wire in the form of a horizontal spiral was used. In this case the wire was fused, i.e., the temperature was not below 1100°C.

Experiments on gelatinized nitroglycerine (97:3) at straight (silver and copper) wires provided the fusing of both wires. Thus, the temperature of the combustion of the gelatinized nitroglycerine was higher than the temperature of combustion of the nitroglycol. With the combustion of trotyl both wires remained nonfused.

Measurement of the temperature of combustion of mercury fulminate in direct proximity to the condensed phase was carried out by Belyayev in the following manner. Experiments were conducted at low pressure when a visible flame is absent; the temperature was measured by a thin (0.05 mm) copper constantan thermocouple, the junction of which before the beginning of combustion touched the surface of explosive. The temperature thus measured is very low and constitutes about 500°C.

According to the tentative estimate of A. F. Belyayev, temperatures of the combustion of some the other priming explosives studied by him are also relatively low, although above the temperature of combustion of mercury fulminate.

Temperatures measured both according to the fusing of the wires and by thermocouples cannot be considered sufficiently reliable, inasmuch as they can be understated as a result of heat losses and overstated as a result of the catalytic action of the metal. If heat losses can be eliminated in their basic parts, for example, by the application of a large diameter of the tube and motionless with respect to the wire of the zone of combustion, then it is difficult to exclude reliably the possibility of catalysis. Under conditions of experiments with nitroesters the predominant effects are apparently, heat losses, since measured temperatures nitroglycol and the nitrocellulose are considerably below those calculated from the equation of combustion.

Thus, the temperatures of combustion of nitroesters at atmospheric pressure, measured according to the fusing of the wires, are much lower than the rated temperatures of detonation in accordance with the fact that combustion under the indicated conditions is less complete than that with detonation.

Temperatures of combustion of the studied priming explosives are considerably lower than temperatures of the combustion of nitroesters.

As a result of heat losses and possible catalysis during combustion, the temperatures measured should be considered, less reliable than those calculated.

It follows, however, to take account also the possibility of distortion with the calculated determination of the temperature of combustion if burnout or secondary reactions during the cooling products of combustion take place.

CHAPTER V

UNSTABLE COMBUSTION OF EXPLOSIVES

In previous chapters we examined the stable steady combustion of [VV] (BB) explosives, i.e., the combustion which occurs in its whole extent evenly with a constant rate determinable by properties of the explosives and by constant external conditions (pressure, temperature, conditions of heat emission and others).

An experiment indicates, however, that under known conditions combustion ceases to be stable, and becomes nonuniform. The change in the rate of combustion can be periodic, and the average rate remains constant (pulsating combustion). The continuous, uniform or pulsating increase in the rate can take place also.

In this case those cases when the change in the rate of combustion occurs as a result of the change in external conditions, for example, because of the pressure rise during the combustion of the explosive in a closed constant volume, as a result of a progressing external heating of the explosive. However, the acceleration of combustion can take place even under invariable external conditions. The disturbance of the stationary state of combustion can be completed by the initiation of detonation.

The question about conditions of the stability of combustion is of great theoretical and practical interest. As was already

indicated, the contemporary engineering application of explosives is based on the existence of their three classes, the main distinction between which consists in the degree of stability of the combustion: minimum for priming explosives, maximum for powders; secondary explosives occupy in this respect an intermediate position. In order to provide the greatest amount of the stability of the combustion of explosives necessary in their use as powders, it is necessary to know those factors which condition the stability of combustion. The same should be said about the prevention of the transition of combustion into detonation with fires in the use of explosives at plants and warehouses.

Unsteady combustion is usually observed with the combustion of explosives in the initial section of combustion.

Finally, the so-called burst explosive, which appears with a relatively slow uniform heating of a certain quantity of explosives up to high temperatures, can also occur as unsteady combustion. A similar kind of phenomenon can occur and, moreover, in large scales with spontaneous ignition of the explosives in industrial apparatuses.

I. General Theory of the Stability of Combustion [236]

With the combustion the explosive is completely or partially transformed into gases. As a result of the low density, especially at high temperatures attainable during combustion, these gases have a volume exceeding many times the volume of the explosive. If combustion occurred in the natural volume of the explosive, then its products would have a very high pressure measured in hundreds of thousands of atmospheres. If the surface of the burning charge is connected to the atmosphere, then gases are expanded and the pressure near the surface of the explosive is much less. However, it nevertheless has a certain finite value,

namely, that which is necessary in order to impart to the gases that amount of motion which they acquire with expansion. This quantity of motion is more, when the rate of the formation of gases is higher, i.e., the rate of combustion, and when the pressure of the environment, upon which the finite density and rate of motion of the expanded gases depends, is less. However, the dynamic increase in pressure in turn affects the combustion, inasmuch as the rate of combustion increases with an increase in pressure. The increase in the rate of combustion, obviously means an increase in the quantity of gases which are formed per unit of time, and, consequently, in the rate of their motion, i.e., the increase in the dynamic increase in pressure. Both these characteristics of the process are thus reciprocally connected. However, the nature of the connection is distinguished. Combustion, i.e., the formation of gases can occur independently of the outflow of the gases, and the outflow of the gases is possible only when they are formed, i.e., if combustion occurs.

The formation of gases and their outflow depends on pressure. The possibility of stable equilibrium between the gas arrival and gas removal, obviously, is determined by the relationship of the rates of their increase with pressure.

If the gas arrival increases with pressure faster than the gas removal, then the stable equilibrium between them cannot be - an increase in the gas arrival will not be compensated by the gas removal. If the gas removal increases faster than the gas arrival, then such a compensation is carried out. These relationships become especially descriptive with their graphic presentation.

As a most simple case let us examine the combustion of a cylindrical charge, which is located in strong tube with a 1 cm^2 cross section and burning on one open end at an external pressure p_0 . The gases of combustion being formed will flow out in a direction opposite to the direction of the propagation of combustion at a rate dependent on the rate of their formation (Fig. 242).

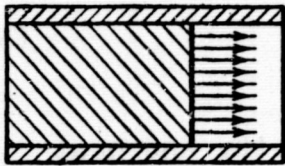


Fig. 242. Diagrammatic representation of the motion of gases during combustion in a tube.

Processes of the formation of gases occurring during combustion and their discharge from the tube depending on the pressure inside the tube are given in Fig. 243. Plotted along the axis of abscissas is the pressure of the surface of the front of combustion. Plotted along the axis of the ordinates are values m_1 - quantity of the gases which are formed at the given pressure in 1 s from 1 cm² of surface of the front of combustion (the mass rate of combustion) and m_2 - the quantity of gases which flow out per unit time at the pressure inside the tube p and external pressure p_0 through each square centimeter of its cross section (flow of gas).

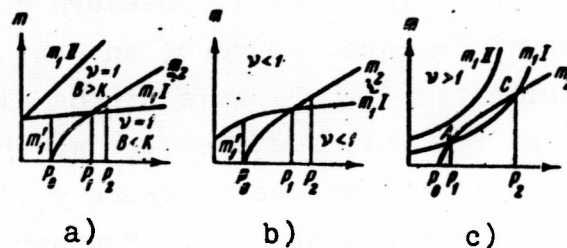


Fig. 243. Dependence of the rate of the formation of gases during combustion and their outflow upon pressure.

The line representing the flow of gas depending on pressure has, as is known from gas dynamics, the following form. When $p = p_0$, i.e., if the pressure of the front is equal to the external pressure, the flow of gas is equal to zero. With an increase in pressure the flow of gas increases, and in the beginning this increase proceeds along the curve, and then, starting from the pressure approximately 2 times exceeding the external pressure, the flow of the gas increases directly proportional to the pressure:

$$m_2 = Kp, \quad (5.1)$$

where K - constant dependent on temperature, density and heat capacity of the gas.

The line of the gas arrival $m_1 = Su_m$ is, in essence, the line which represents the mass rate of combustion as the function of pressure, since S is the area of the surface of combustion which we accepted equal to one. In conformity with dependence fulfilled for many explosives

$$u_m = A + Bp$$

let us plot on graph a, Fig. 243 for m_1 two straight lines I and II, by two values B : $B < K$ and $B > K$.

It is easy to show that when $B < K$ a combustion will be stable. Actually, if we ignite the explosive at pressure p_0 , then at this pressure the gas removal is equal to zero, and the gas arrival is represented by the ordinate m'_1 . Because of the difference in the gas arrival and the gas removal, the pressure at the front of the combustion increases until it reaches pressure p_1 , at which the gas removal becomes equal to the gas arrival. Further with $B < K$, the pressure cannot increase, since at high pressures the flow of gas is more than the gas arrival. Therefore, if the pressure for any random reason increased, for example, up to value p_2 , it inevitably should then be lowered to value p_1 .

Since K at the given composition of gases is a constant magnitude, then the gas-dynamic stability of combustion depends on value B (more accurately du/dp) with equilibrium pressure. The less B , the more the stability. Thus, the independence of the rate of combustion on pressure ($B = 0$), and all the more so, its decrease with an increase in pressure ($B < 0$) give the greatest stability of combustion. Let us recall that the first dependence ($B = 0$) was observed in the definite region of pressures for a number of quick-burning explosives,

and the second ($B < 0$) - for potassium picrate and of some other salts similar to it.

It is easy to show that with $B > K$ the pressure in the tube will continuously increase, and stable equilibrium between gasification and gas removal cannot be established at any pressure.

The plotting of appropriate graphs of the dependence of the rate of combustion upon pressure $u_m = A + Bp^v$ when $v < 1$ and when $v > 1$ (Fig. 243, graphs b and c) indicates that in the first case combustion can be either unstable at all pressures, when the curve of gas arrival II is located wholly over the line of the gas removal, or at some interval of pressures (up to $p = p_2$, curve I of graph c) the combustion can be stable and at high pressures - accelerating.

Let us emphasize that the equality of the gas flow and gas arrival is not sufficient for the stability of combustion. This is visually evident on graph Fig. 243.

At point A the gas arrival and gas flow are equal, and their equilibrium is stable, since if pressure would rise, then the gas flow would stop more than gas arrival, and the pressure would drop again down to p_1 .

Otherwise the matter is at point C , where the gas flow and gas arrival are also equal. If the pressure drops below p_2 , then it will continue to fall, since in this interval of pressures the gas arrival is less than the gas flow. On the contrary, if the pressure rises somewhat above p_2 , then it will continue to increase, since the gas arrival will be more than the gas flow. Thus, deviation from the equilibrium in both directions will not cause return to it but further intensification of the initial deviation. This denotes instability of the equilibrium.

Thus, the possibility of a stable combustion at the given pressure is determined by a relationship between the rate of combustion (more accurately the rate of gasification) and by the rate of the departure

of gases at this pressure, or, more correctly speaking, by the relationship between the acceleration of the gas arrival and acceleration of gas flow with pressure.

If with the equality of the gas arrival and gas flow, the gas arrival increases with pressure more rapidly than does the gas flow, then combustion is unstable, and, conversely, if the gas arrival increases more slowly than the gas flow, then we have a stable combustion.

Consequently, with the examined gas-dynamic approach to the question about the stability of combustion, this stability should be determined by values of quantity K - the tangent of the angle of inclination of the straight line of the gas arrival and quantity $B = du_M/dp$ - the derivative of the rate of combustion (more accurately, rate of gasification) with respect to pressure. Inasmuch as these or other parameters (for example, pressure, temperature, relative density) affect B or K , then they will affect the stability of combustion.

On the basis of these general considerations about the condition of the stability of combustion, we will examine the available data in reference to the specific explosives and to specific conditions of combustion.

The gas flow at increased pressures, as was indicated, is directly proportional to the pressure. The coefficient of proportionality

$$K = \sigma \sqrt{\frac{k}{k+1} \left(\frac{2}{k+1}\right)^{2/k-1}} \sqrt{\frac{2T_0}{p_0 v_0 T_1}} = \sigma \sqrt{\frac{k}{k+1} \left(\frac{2}{k+1}\right)^{2/k-1}} \times \\ \times \sqrt{\frac{2T_0 M}{p_0 22410 T_1}} = \sigma \sqrt{\frac{k}{k+1} \left(\frac{2}{k+1}\right)^{2/k-1}} \sqrt{\frac{2 \cdot 273 M}{1.013 \cdot 10^6 \cdot 22410 T_1}}, \quad (5.2)$$

where σ - cross section of the opening for the outflow of gases (cm^2), and $k = c_p/c_v$; M - molecular weight of the gases (in g); p_0 - atmospheric pressure - $1.013 \cdot 10^6$ dyn/cm²; v_0 - the specific volume of gases (into cm³/g); T_0 - 273°K; T_1 - temperature of the gases (in °K).

For diatomic gases

$$\sqrt{\frac{k}{k+1} \left(\frac{2}{k+1}\right)^{2/k-1}} = 0,485$$

and

$$K = \sigma 0,485 \cdot 0,0001555 \sqrt{\frac{M}{T_1}} = 0,0000752 \sigma \sqrt{\frac{M}{T_1}}.$$

From the equation it is evident that K is not strictly a constant quantity but can be changed, respectively, to different possible values of the temperature of gaseous products of combustion and of their molecular weight. For an estimate of quantity K necessary for comparison of the theory with the experiment, let us calculate its value, having accepted for simplicity that $\sigma = 1$, the temperature of combustion is equal to 2730°K, and the average molecular weight of the gases is equal to 28 (carbon monoxide and nitrogen). Then the numerical value K is equal to ~ 7.4 (g/s cm²): (kg/cm²).

At increased temperatures value K somewhat decreases according to a decrease in c_p/c_v ; if the explosive (for example, mercury fulminate) forms heavy gases, quantity K becomes more. If combustion occurs with dispersion, so that only the part of the condensed explosive turns into gases, then quantity K decreases, since the rate of the motion of the gases decreases.

To estimate the stability of combustion, it is necessary to compare value K with value du_M/dp from the expression of the dependence of the rate of combustion upon pressure (Table 41). If this dependence during normal combustion is linear, du_M/dp is constant, which we designated as B . If dependence $u(p)$ is different, then du_M/dp was calculated graphically for the definite interval of pressure.

For all the studied secondary explosives values of du_M/dp are much (50-200 times) less than the maximum value, starting from which stable combustion is gas-dynamically impossible. Thus, the capacity

of secondary explosives for stable combustion is theoretically quite natural.

Table 41. Value of the derivative of the mass rate of combustion on pressure (du/dp).

Explosive	du/dp , g/s·cm ² /kg/cm ²	Explosive	du/dp , g/s·cm ² /kg/cm ²
Collodion.....	0.0162	Tetryl.....	0.0513
PETN.....	0.0180	Liquid methyl nitrate liquid.....	0.1330
Gelatinized nitroglycol....	0.0290	Gelatinized nitroglycerine... ..	0.1460
Liquid nitro- glycol.....	0.0390	Mercury fulminate...	4.18
Pyroxylin No. 1	0.0405	Trinitrotriazidobene	0.85
Hexogen.....	0.0505		

Those of the priming explosives, which in a state pressed to a great relative density are capable of stable combustion, are characterized at low pressures by a greater dependence of the rate of combustion upon pressure than are the secondary explosives; value du_M/dp for them approaches the maximum.

At increased pressures for the priming and quick-burning explosives studied in this respect, the ratio du_M/dp decreases; however, the rate of combustion according to absolute value is great, and, consequently, the dynamic increase in pressure is also great.

It is possible that those priming explosives for which it was not possible to observe experimentally a stable combustion are characterized by even larger values of du_M/dp , which also should lead to the impossibility of stable equilibrium between the gas arrival and gas removal, in other words, to the impossibility of a stable combustion.

However, the great dependence of the rate of normal combustion upon pressure is not the only possible reason for the instability of the combustion. The mass rate of combustion is equal to its normal rate, multiplied by the effective surface of the combustion. Thus far it was proposed that the surface of combustion is equal to the area of the end of the burning charge. In actuality, this is not necessarily so - the surface of combustion can become considerably more. This is carried out, for example, if combustion occurs with intense dispersion, and the actual surface of combustion is as many times more than the cross section of the charge as the total surface of the particles is more than the area of the end of the charge. Dispersion can have not only a chemical nature (gas-forming reaction in the condensed phase) but also a physical one - particles of explosives can be formed as a result of the powerful splitting of its crystals under the effect of a thermal shock, as a result of the liberation of vapors of highly volatile admixtures or gaseous inclusions, etc.

The increase in the surface during combustion is especially natural if explosive is characterized by considerable gas permeability and combustion occurs in a layer of some finite thickness. Such convective combustion differs not only by the considerably greater rate, than the normal, i.e., by much greater Δp , but also by a much greater du_M/dp , inasmuch as this ratio in this case is determined not only not so much by the relatively weak dependence of the normal rate of combustion upon pressure as by the much greater dependence of the thickness of the burning layer (the surface of combustion) upon pressure. This thickness is determined Δp , which is small in comparison with p ; therefore, a small change in pressure which changes the rate of normal combustion little, will be large with respect to Δp , will greatly change the thickness of the burning layer and du_M/dp .

The few available data indicate rather in favor of the fact that the acceleration of combustion of the priming explosives, which leads to its transition into detonation, is conditioned by not an extremely

great dependence of the normal rate of combustion upon pressure¹ but by the increase in the surface of combustion in one of the ways shown above. A number of features of the priming explosives, specifically, the high temperature and high rate of combustion at low pressures, which condition the increased tendency of their combustion toward a transition into a convective mode, facilitate the transition of combustion into detonation.

Thus, one of the fundamental facts which characterize explosives – the stability of the combustion of secondary explosives and the instability of combustion of initiating explosives – is naturally explained in theory.

However, it is known that the combustion of secondary explosives, in most cases stable, under some conditions turns into detonation. In exactly the same manner those priming explosives which, according to the gas-dynamic criterion, should burn stably and thus actually burn under definite conditions, for example, under a greatly pressed state, in a vacuum, under other conditions, for example, at lower pressures of pressing, give a rapid transition of the combustion into detonation.

From the point of view of the theory, the formation of the transition of combustion into detonation in both cases should be interpreted as a result of the change in the dependence of the rate of combustion upon pressure to the side of an increase in du_m/dp . In order to explain how this change occurs, let us examine sequentially experimental data on the combustion of liquid explosives and powdery explosives under those conditions when the steady flow of the process

¹Thus, for instance, for mixtures of lead of azide with liquid secondary explosives under conditions of normal combustion, the rate of it is only somewhat more than the secondary explosives. For mercury fulminate in a greatly condensed state at high pressures, the rate of normal combustion increases even more slowly than it does at low pressures.

is disturbed and the theoretical interpretation of this disturbance.¹

II. Effect of Pressure, Temperature and Physical Features on the Stability of Combustion of Liquid Explosives

Theory of the Stability of Combustion of Explosive Fluids

In Chapter three we examined experimental data on steady combustion of a number of liquid explosives — methyl nitrate, nitroglycol, nitroglycerine and others. However, the combustion of all these substances is steady and uniform only under definite conditions. The basic of these conditions are the pressure and temperature at which combustion occurs. A substantial role is also played by the viscosity of the liquid.

Experimental investigations [237] gave the following general picture of the effect of various factors on the nature of the combustion.

If the pressure lies lower than a certain limit, then the combustion is not propagated. This lower limit is conditioned by the thermal losses of reactive layer both into the environment and into the thickness of the explosive and depends, therefore, upon the diameter of the charge, properties of the material, walls of the shell, etc. At pressures higher than the lower limit combustion is stable, and its rate increases with an increase in pressure. Observation of combustion indicates that the surface of the liquid, remaining horizontal and apparently calm, is moved downward. At a certain pressure different for different explosives the nature of the combustion is changed — it becomes pulsating. This fluctuation is different in its nature for different explosives and under various conditions of

¹Examined below are experimental data only with respect to the unstable combustion of liquid explosives. K. K. Andreyev did not have time to write the section on the instability of the combustion of powdery explosives (besides that part of experimental data on the combustion of powders, which are available in Chapter 3, page 186 and further) (editor's note).

combustion. During the combustion of nitroglycerol the surface of the liquid begins as if it vibrates, and the period of pulsation and amplitude of the vibrations of the surface are small.

In methyl nitrate the nature of the pulsation is the same, but the amplitude and period of vibrations are considerably more. In nitroglycerine at the usual temperature pulsation occurs in a form resembling a flash, is accompanied by the spilling of the liquids, and usually leads to the extinguishment of combustion. The nature of the pulsation of liquid explosives is also affected by the initial temperature.

The magnitude of the pressure at which combustion turns into a pulsation mode, and values of the rate of combustion are different for different explosives. Thus, for methyl nitrate this occurs at 1.75 at, and the rate of combustion is about $0.26 \text{ g/cm}^2\text{s}$, and for nitroglycerol the pulsation combustion approaches at 17 at and rate of combustion of $0.79 \text{ g/cm}^2\text{s}$, for nitroglycerine ($t = 98^\circ\text{C}$) - at 0.4 at and a rate of combustion of $0.12 \text{ g/cm}^2\text{s}$.

The increase in temperature facilitates the formation of pulsation, lowering the pressure at which it starts.

Figure 244 gives results of experiments of I. A. Tereshkin on the effect of temperature on the value of pressure of the transition of the combustion of nitroglycerol into a turbulent mode and the dependence of the rate of combustion in this mode upon pressure.

When pulsation leads to the extinguishment of combustion, the increase in temperature impedes this extinguishment, leading to an increase in the pressure of the extinguishment or even completely preventing it. Thus, for the liquid and weakly gelatinized nitroglycerine at a usual temperature there occurs extinguishment, at moderately increased temperature - combustion occurs with pulsation, and at greatly increased temperature - an explosion appears. For a methyl nitrate the increase in temperature leads to the fact that instead of a uniform pulsation an explosion appears.

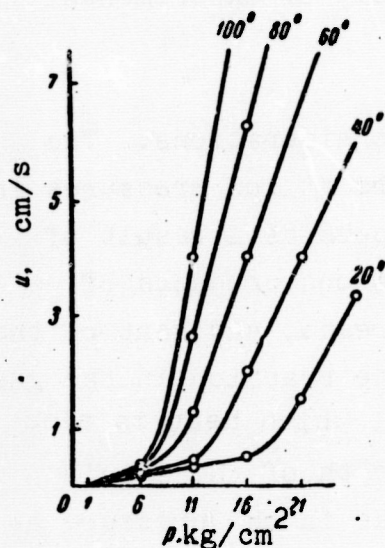


Fig. 244. Dependence of the rate of combustion of nitroglycol upon pressure at various temperatures.

The increase in the viscosity of the liquid impedes the initiation of pulsation. Thus, if liquid nitroglycerine does not burn at atmospheric pressure, nitroglycerine, gelatinized by dissolution in it of a high-polymer substance, normally burns both at atmospheric and at moderately increased pressures. In this case the higher the viscosity of the gelatin, the higher the pressure at which combustion turns into a pulsating mode or is extinguished. The fact that the stabilizing effect of the gelatinizing of addition is connected with the increase in viscosity indicates the absence of this effect with the addition of the same substance not in the form of a polymer but in the form of a monomer.

The behavior of nitroglycol is similar: the combustion of liquid nitroglycol passes over to a pulsation mode at a pressure of about 20 at, and the slightly gelatinized (97:3) substance burns evenly even at 150 at.

This is basically the general picture of the disturbance of the uniformity of combustion and the effect on the formation of this disturbance of various factors.

A theoretical analysis of the disturbance of the normal nature of the combustion of liquids was given by Zel'dovich [238] on the

basis of the view of Belyayev and (independently of experimental investigation) Landau [239].

Zel'dovich proceeds from the following considerations. The combustion of volatile liquid explosives occurs at low pressures in such a way that the liquid¹ is turned into vapors as a result of heating by means of heat transfer from the gaseous products of reaction. The vapors, being heated further, react, and heat of the reaction is liberated. However, along with the reaction in the gas phase there occurs a reaction in the liquid at which heat is also liberated, in consequence of which into the depth of the liquid a thermal wave is propagated. With an increase in the pressure at which combustion occurs, the rate of the reaction in the gas phase and, respectively, the rate of combustion are increased. However, simultaneously increases the rate of reaction in the liquid phase, since with an increase in pressure the temperature on the surface of the fluid equal to the temperature of its boiling increases.

With definite relationships between magnitudes of the energy of the activation and the heat of vaporization of a liquid explosive, the rate of the wave of heating, which propagates in the liquid during combustion, increases with pressure more rapidly than the rate of combustion. Therefore, starting from a certain maximum pressure, the rate of the wave of heating can become more than the rate of combustion. Then instead of vaporization of the liquid on the surface of combustion there occurs its effervescence in the layer of a certain finite thickness, which leads, on one hand, to a sharp increase in the surface of the burning liquid and, on the other, to the admission of bubbles of vapor from the liquid into the zone of hot gaseous products of combustion and ultimately to the great increase in the quantity of substance which burns per unit time, which leads to detonation.

Zel'dovich gave the expression for maximum pressure p_{np} , which

¹In essence these considerations are applied to a solid explosive, which melts during combustion before conversion into vapors.

allowed approximately calculating its values for nitroglycol and methyl nitrate [240]. However, these calculations gave values of maximum pressure exceeding by several orders, its experimental values. Furthermore, as Zel'dovich himself indicates, the relationships isolated by him are applicable only when p_{np} is considerably lower than the critical pressure, which for nitroglycol, although it is not established, by analogy with other substances does not exceed considerably 50 at. Therefore, the obtained values of maximum pressure do not have a physical meaning.

It follows, however, to show, that the data used during the calculation on the heat of the reaction are calculated from the composition of the gaseous products of a combustion and are not directly determined for the reaction in the liquid phase; furthermore, during the calculation the magnitude of maximum pressure to a great degree depends on the ratio of the rate of combustion to the rate of the thermal wave. The rate of combustion, as the experiment indicates, depends on the viscosity of the liquid, which in theory is not considered. Further reaction in the liquid phase is accompanied by the liberation of bubbles of gas mixing it which can affect the coefficient of the heat transfer. Because of these possible sources of an inaccuracy, the quantitative divergences of results of the calculation and experiment themselves do not have a decisive importance.

A known additional possibility of checking the hypothesis is the comparison of the temperature dependence of maximum pressure which results from it, with the experimental. In equations of Zel'dovich, the change in maximum pressure with temperature depends on the change with the temperature of the rate of combustion and rate of the thermal wave. The latter is proportional to the ratio $\frac{1}{T_x - T_0}$, i.e., it relatively weakly increases in the region of low temperatures and greatly increase with the approach of the initial temperature to the boiling point. Inasmuch as the rate of combustion of nitroglycol increases with pressure more evenly and slowly, the maximum pressure decreases with the increase in the initial temperature in the beginning slowly, and then increasingly more and more and rapid. With

the transition from 20° to 100°C the maximum pressure decreases 3.5 times with respect to the calculation, which agrees with the experiment. At higher temperatures the calculation gives a greater decrease in maximum pressure than that which, apparently, takes place in actuality.

In the examined mechanism of the formation of the explosion there is, however, one fundamental questionable moment. It consists in the fact that the reaction in the gas phase is considered independently of the reaction in a liquid. At the same time it is obvious that the acceleration of the exothermic reaction in the condensed phase will lead also to the acceleration of combustion in the gas phase, and the discontinuity between both rates will not be obtained.

Apparently, the presence of an apparent reaction in the liquid will lead only to a certain acceleration of combustion in comparison with the case when the reaction in the condensed phase is absent and by itself cannot lead to an explosion. In favor of this is the experimental fact that the nonvolatile substances, for example, pyroxylin, whose reaction knowingly occurs also in the condensed phase, burn quietly (without transition into an explosion) in the very large interval of pressures. This refers also to the many volatile explosives which burn at increased pressures, i.e., at a high boiling point.

The hypothesis of Zel'dovich considers the increase in pressure as the factor which stimulates the transition in the combustion into an explosion. There are, however, observations which indicate the possibility of the initiation of an explosion with a rapid decrease in pressure over the burning liquid, which leads to its effervescence. Thus, Belyayev observed in these conditions the transition of the combustion of methyl nitrate into an explosion. With the interpretation of these results one should take into account the great tendency of vapors of methyl nitrate and their mixtures with air to explode with combustion [241] and also low stability of the combustion of methyl nitrate itself, which already at a pressure of about 2 atm turns into an excited mode.

An explosion with the effervescence of the hot liquid can appear also for the following reason: during combustion the tube is heated, evacuation leads to stormy effervescence of the small quantity of the liquid being used, and vapors appear in the heated tube and, in being heated, explode. At large quantities of the liquid it would be possible to expect the extinguishment of combustion as a result of the excessive admission of the cold liquid into the zone of combustion and the drop in temperature of the gases.

The formation of an explosion as a result of the effervescence in general is highly improbable because the acceleration of combustion as a result of boiling will cause an increase in pressure, and the increase in pressure will suppress the boiling. Thus, the acceleration of combustion as a result of the effervescence should be, as a rule, a self-stopping process, and only in specific cases when the acceleration of combustion occurs very sharply¹ can it lead to detonation.

The fact that the state of boiling by itself is not a sufficient condition for the transition of combustion into detonation is evident from that fact that the many explosives, the boiling point of which lies below the flash temperature, do not provide detonations with a flash [242]. It is obvious and proved by direct observation that spontaneous ignition at atmospheric pressure approaches for the indicated substances in the boiling state.

Another mechanism of the acceleration of combustion of liquid explosives was advanced Landau [239]. He indicated that the normal "heat conductivity" mode of combustion, which consists in the vaporization of the liquid, heating and chemical reaction in vapors, is, generally speaking, unstable. The disturbance which appears in the front of such a combustion strives to be increased in amplitude with time. The higher the rate of combustion, the less the stability of the plane front of combustion.

¹In this case a substantial role can be played, as Belyayev indicates [243], by the heating and combustion of the vapor bubbles as a result of their isentropic compression.

Factors which prevent distortion of the front are the force of gravity, surface tension and viscosity of the liquid. Stabilization of combustion can be provided also by the small magnitude of the diameter of the tube. If the disturbances of the normal mode of combustion take place, then they are expressed in the turbulization of the front of combustion, which leads to an increase in the quantity of the burning substance by a unit of area of the cross section of the column of liquid.¹

The account of the stabilizing effect of the gravity and surface tension leads to the following expression for the maximum rate of combustion, which allows a normal undisturbed combustion:

$$\dot{u}_m = (4\alpha_k g \rho_r^2 \delta_m)^{1/4}, \quad (5.3)$$

where \dot{u}_m - the mass rate of combustion ($\text{g}/\text{cm}^2\text{s}$); α_k - surface tension between the liquid and its saturated vapor at the boiling point (dyn/cm); ρ_r - density of the gaseous products of combustion (g/cm^3); δ_m - density of the liquid (g/cm^3).

If the rate of combustion exceeds the value calculated from equation (5.3), then the combustion can, nevertheless, be stable if the liquid is in a container of quite small diameter (d). The condition of stability in this case has the form

$$d < \frac{\alpha_k \rho_r}{\dot{u}_m^2}. \quad (5.4)$$

The calculation usually shows that condition (5.4) gives even during combustion under atmospheric pressure and all the more so at increased pressures to very small values of diameter. In the usual conditions of the experiment combustion in such thin tubes is not

¹In principle this mechanism of the increase in the rate could take place even during the combustion of solid melting explosives. However, the small thickness of a molten layer (especially at high pressures) prevents in this case the possibility of the acceleration of combustion as a result of turbulization.

propagated because of thermal losses.

Expression (5.3) can be transformed [244], having made use of the approximation relation for the parachor

$$P = \frac{M\alpha^{1/4}}{\delta_{\pi}}. \quad (5.5)$$

where M - molecular weight.

For the critical mass rate of combustion we obtain the expression

$$u_n = 7.91 \frac{P}{M} \rho_r^{1/2} \delta_{\pi}^{1/4}. \quad (5.6)$$

For the critical linear rate

$$u = 7.91 \frac{P}{M} \rho_r^{1/2} \delta_{\pi}^{1/4}, \quad (5.7)$$

The use of expression (5.6), although it is somewhat less accurate, for the characteristic of the stability of combustion, is especially convenient because the magnitude of the parachor can be calculated from the structural equation of the substance and is not changed with temperature in the wide interval of the change in the latter. Thus, it is possible to avoid the experimental determination of the surface tension of the explosive at the boiling point, which in most cases in practice is unrealizable; for many explosives even the boiling points themselves, especially at increased pressures are unknown and difficult to determine.

Apart from this, expression (5.6) allows evaluating the effect of the chemical structure of the liquid explosive on the stability of normal combustion and indicating that the value of the maximum rate for various explosives is changed within very narrow limits.

Actually, factor P/M physically corresponds to the specific volume of the substance at the temperature at which $\alpha = 1$. Densities of liquid organic explosives consist at the usual temperature in the interval in 1.2-1.6 g/cm³. Correspondingly, values P/M are little

distinguished, inasmuch as the composition of various organic explosives (correlation C, H, N and O) is changed little.¹ This conclusion can be illustrated by the data of Table 42.

The quantity $\delta_{\text{ж}}^{\text{ж}}$, according to the small interval of the change in $\delta_{\text{ж}}$, is changed little, and all the more so $\delta_{\text{ж}}^{\text{ж}}$ if we speak about the linear rate of combustion.

The density of the gas products of combustion

$$\rho_r = 273/v_0 T_r, \quad (5.8)$$

where v_0 - the volume of the gaseous products of combustion of 1 gram of the substance under normal conditions; T_r - temperature of combustion.

A certain change in ρ_r is possible because of the change in the equation of the reaction of combustion with the change in pressure. However, this change is small, as it is easy to show in the example of an explosive with high caloricity, at which the effect of the change in the equation of combustion should be especially considerable. With the combustion of nitroglycol up to products of complete conversion, not allowing for dissociation, ρ_r would be equal to about $8.6 \cdot 10^{-5} \text{ g/cm}^3$. With the combustion of nitroglycol at atmospheric pressure, according to data of the experiment, $\rho_r = 1.87 \cdot 10^{-4} \text{ g/cm}^3$. Thus, for the greatest change in the equation of combustion, which exceeds that possible in actuality, ρ_r is changed only 2.2 times and $\rho_r^{\text{ж}}$ 1.5 times. There is no basis to expect a substantial difference between ρ_r for different organic explosive liquids. For methyl nitrate, nitroglycol, and nitroglycerine, the values calculated from the experimentally determined composition of the products of combustion

¹A considerable increase in P/M is observed only for substances or mixtures rich in hydrogen ($P/M = 17.1$), for example, hydrazine a solution of methanol in hydrogen peroxide and methane in oxygen, and so on. However, for such substances the effect of the large magnitude of the ratio P/M by the magnitude of critical rate will, to a certain extent, be compensated by a decrease in the density of the products of combustion.

Table 42. Values of the parachor and ratio P/M for various explosives.

Explosive	Parachor P*	Molecular weight	P/M	Explosive	Parachor P*	Molecular weight	P/M
Methyl nitrate..	149.1	77	1.94	Trinitrobenene....	374.8	213	1.76
Nitroglycol.....	264.0	152	1.74	Trinitrotoluene...	413.8	227	1.82
Nitroglycerine..	378.9	227	1.67	Picric acid.....	394.8	229	1.72
Pentaerythritol tetranitrate...	532.8	316	1.68	Trinitrophenyl- metylnitramine (tetryl).....	499.3	287	1.74

*Values of the parachor and molecular weight in all cases are calculated.

were respectively, $1.93 \cdot 10^{-4}$, $1.87 \cdot 10^{-4}$ and $1.72 \cdot 10^{-4}$ g/cm³.

From the aforesaid it results that the right-hand side of the equality can actually be considered as approximately a constant (~ 0.25 g/cm²·s at atmospheric pressure).¹

Hence it follows that the stability of normal combustion can be characterized by the magnitude of the rate of combustion under the given conditions of pressure and temperature.

The rate of combustion should be determined experimentally. However, in principle it can also be calculated theoretically, on the basis of the theory of Zel'dovich-Belyayev, if the thermochemical and dynamic characteristics of the leading reaction of combustion under determined conditions of the latter are known.

Equation (5.6) shows the dependence of the maximum rate upon pressure at which the combustion occurs. With the change in pressure in the right-hand side of the equation basically only the density of the gases proportional to the pressure is changed. Taking this dependence into account, we obtain

$$u_{M(\kappa p)} = \beta p^{1/2}, \quad (5.9)$$

where $\beta = 0.25$, if we express p in atmospheres and $u_{M(\kappa p)}$ in grams per square centimeter per second.

Thus, the condition of the stability of the normal combustion of the liquid can be formulated in the following manner: if the rate of combustion at a given pressure is more, then the combustion is unstable, and vice versa. From expression (5.9) it also follows that

¹Values $u_{M(\kappa p)}$ calculated on the basis of experimental data for α_k , ρ_l and δ_w for a methyl nitrate, nitroglycol and nitroglycerine were, respectively, 0.26, 0.26 and 0.25 g/cm²s.

with an increase in pressure the stability of combustion decreases.

Actually, the rate of combustion can be assumed to be approximately proportional to the pressure. Thus, with an increase in pressure the rate of combustion increases more rapidly than the calculated value of maximum rate, and at some pressure the rate of combustion becomes equal to the maximum value. This pressure can be determined from the following relation. Assuming that $u \approx Bp$, we obtain

$$Bp_{kp} \approx \beta p^{1/2}$$

or

$$p_{kp} \approx \left(\frac{\beta}{B}\right)^2. \quad (5.10)$$

The calculated value p_{kp} will usually be overstated, since the experiment indicates that at pressures considerably lower the rate of combustion starts to increase with the pressure not in proportion to it more rapidly. Furthermore, examined relations and, specifically, the constancy of the maximum rate retain their correctness only until the pressure at which combustion occurs is too close to the critical pressure. Under these last conditions the surface tension of the liquid becomes equal to zero, and the value of the maximum rate, determined by expression (5.6) drops accordingly to zero.

Inasmuch as the critical pressure of organic explosive liquids is equal, as the experiment shows to $\sim 50 \text{ kg/cm}^2$, one can conclude that the stable combustion of liquids above 50 kg/cm^2 should be impossible. Therefore, with an increase in pressure (especially with an approach to the critical) the rate of combustion should increase more rapidly because of the Landau effect; furthermore, pulsation should appear. These facts do not exclude, however, the possibility of the stable flow of combustion, and with a small period of the pulsation, even its apparent uniformity.

Equation (5.6) shows the effect of the initial temperature of the explosive on the stability of its combustion. Its right-hand side barely depends on temperature (more accurately, it very slightly decreases with temperature according to the decrease in the density of the liquid). The left side of the equation (the rate of combustion) increases with temperature; in other words, the stability of the combustion should decrease with an increase in the initial temperature.

There is, however, a difference in the effect of pressure and temperature. We can increase the pressure unlimitedly, right up to its values which correspond to an unstable combustion for any liquid; the possibility of an increase in temperature is limited to the temperature of spontaneous ignition of the substance. Therefore, it is possible by this last way to arrive at an unstable combustion not for any liquid explosive.

Above we determined that the achievement of the critical rate leads to the stopping of the mode of normal ("thermal conductivity") combustion. The question about what consequences the bending of the plane surface of the front will have is not dealt with in detail by the theory.

Bending, in other words, the increase in the surface of the contact of the gases and the liquid, should entail the intensification of the heat exchange between the products of combustion and the liquid and, because of this, the acceleration of vapor generation and combustion. However, this acceleration is limited by that fact that the quantity of heat separable during combustion is limited by the rate of the chemical reaction in the gas layer, where the reaction occurs, and by the area of its surface (surface of the initial flame). If the kinetic and thermochemical constants of the reaction in the gas phase are such that the hot gases are in a state to "overboil" intensely the entering vapors, in other words, if the acceleration of the vapor generation behaves as the acceleration of the chemical reaction in the gases (per unit of cross section of the tube) as a result of the increase in the surface of combustion of vapors or turbulization of the zone of the reaction, then the combustion can be

accelerated. Otherwise, combustion from the beginning is somewhat accelerated, but as a result of the intensification of vapor generation the layer of vapors becomes thicker, drives out the hot zone from the surface of the liquid and therefore decreases the quantity of heat transferred to it by gases per unit time. At the same time with the bending of the surface of the liquid, to a greater or lesser extent its heated frontal layer is thinned, which leads to intensified heat emission into the depth of the liquid. As a result of all of this, the acceleration of the vapor generation is in this case self-stopping (this consist in, specifically, the possible reason for the formation of the pulsation, which is accompanied by the approach of the secondary flame to the surface of the liquid).

The braking of the combustion after its temporary acceleration can be so considerable that the combustion is extinguished, as was observed for some liquids. Conditions for extinguishment are especially favorable if turbulization appears at low pressures, when a secondary flame is absent and the heat release of combustion is little, as takes place, for example, during the combustion of nitroglycerine. At higher pressures, when there is a secondary flame, turbulization leads to a great increase in the rate of combustion, since the increased quantity of vapors being formed is burned in the secondary flame.

A substantial role in this mode of the combustion of the liquids can be played by the transition into the turbulent mode of the secondary flame, inasmuch as with turbulization of the liquid the rate of the motion of the vapors and of products of the initial combustion becomes so considerable that even in narrow tubes used the Reynolds number exceeds the critical value. For nitroglycol, according to the approximation calculation at 25 at $Re = 3200$.

Thus, the acceleration of gasification because of turbulization of the surface layer of the liquid simultaneously leads to the transition of the motion of the gaseous products from lamellar into the turbulent mode. This fact sharply increases the rate of the secondary gas-phase combustion and approaches its zone to the surface of the liquid. The heat separable in the secondary flame is transferred

now to the surface of the liquid no longer by thermal conductivity through the relatively thick layer of gases and of vapors but by convection, and the rate of the combustion of the liquid corresponds not to the temperature of the initial flame but to a much higher temperature of the secondary flame.

The acceleration of combustion as a result of the turbulization of the secondary flame can be a substantial factor not only of the acceleration of combustion and its transition in an explosion, but also of the stabilization of combustion with respect to the formation of the explosion. An experiment indicates that the tendency toward the formation of an explosion during combustion is more in the region of intermediate pressures between the normal and turbulent combustion. Its probable reason is the accumulation in the gas phase, as a result of the turbulization of the liquid, of a large quantity of products of incomplete combustion with liquid droplets suspended in them, the subsequent explosion of which induces a pressure jump, which causes an explosion of the unburned part of the liquid. The acceleration of combustion of intermediate products as a result of the turbulization of the secondary flame prevents their accumulation and makes the combustion more uniform. Really, in the transient region relative great oscillations in the rate of combustion are observed; at greater pressures combustion becomes much more uniform.

We examined the basic conclusions of the theory of the stability of the combustion of liquids. To what degree do experimental data agree with them?

Such data were obtained during the study on the combustion of four liquids: methyl nitrate, nitroglycol, diglycoldinitrate and nitroglycerine. All these substances burn at room temperature and atmospheric pressure. The rate of combustion of nitroglycerine is 0.23, methyl nitrate - 0.14, nitroglycol - 0.044 and diglycoldinitrate - 0.021 g/cm²s, i.e., it is less than the critical value (0.25 g/cm²s). Consequently, according to theory, the combustion of these substances can be stable. The rate of the combustion of nitroglycerine is very close to the critical. The limited capacity

of nitroglycerine for normal combustion is a natural consequence of the relatively high rate of combustion.

At increased temperatures (60°C) the combustion of methyl nitrate turns into an explosion; the maximum calculated rate of combustion for it is $0.24\text{ g/cm}^2\text{s}$; the rate determined by the extrapolation of experimental results at this temperature is equal to $0.20\text{ g/cm}^2\text{s}$. For nitroglycol the rate of combustion near the temperature of spontaneous ignition is equal to $0.09\text{ g/cm}^2\text{s}$, and in this case it does not explode; the maximum rate according to calculation is $0.25\text{ g/cm}^2\text{s}$. Thus, the effect of temperature on the stability of the combustion of both nitroesters also agrees with the theory.

During combustion under increased pressures for methyl nitrate (starting from 1.75 at), for nitroglycol (from 19 at) and for diglycoldinitrate (from 55 at), the change from uniform combustion into an accelerated pulsating combustion is observed. Values of calculated rates of stable combustion are $0.32\text{ g/cm}^2\text{s}$ for methyl nitrate and $0.88\text{ g/cm}^2\text{s}$ for nitroglycol; experimental rates are between 0.26 and $0.46\text{ g/cm}^2\text{s}$ in the first case and about $0.90\text{ g/cm}^2\text{s}$ in the second case. For diglycoldinitrate the critical rate is about $0.7\text{ g/cm}^2\text{s}$, which is considerably less than the calculated value. This fact is not astonishing, since for diglycoldinitrate the transition of combustion from a normal into an excited mode occurs near the critical pressure (in the value of this term accepted in physical chemistry) when the surface tension (and, consequently, critical value of the rate of combustion) tends toward zero.

For nitroglycerine at atmospheric pressure the rate of combustion, as it was mentioned, is close to that permissible for stable combustion. According theory, one should conclude that at reduced pressure nitroglycerine should burn. Actually, as we have seen, at pressures of 100-200 mm nitroglycerine burns; if combustion occurs in a closed container and the pressure of the gases increases, then upon reaching a pressure somewhat higher than 300 mm combustion is extinguished. The calculated value of the maximum rate at 310 mm is $0.16\text{ g/cm}^2\text{s}$, and the actual magnitude of the rate near extinguishment is less and

consists of $0.12 \text{ g/cm}^2\text{s}$. At increased temperatures instead of the extinguishment, combustion with an increase in pressure turns into a pulsating mode, which sometimes leads to extinguishment. The maximum rate of combustion without apparent pulsation is $0.21 \text{ g/cm}^2\text{s}$, i.e., more theoretically permissible.

Thus, the theoretical conclusions and experimental data with respect to the possibility of the stable combustion of a number of liquid explosives at atmospheric pressure and the effect of temperature and pressure on the stability of combustion on the whole agree well with each other.

The theory of Landau examines the stabilization of combustion due to forces of the surface tension and gravity.¹ A similar effect should prove to be the viscosity of the liquid. Gelatinized nitroglycerine burns stably in the large interval of pressures [245]. In experiments under increasing pressure at which the liquid nitroglycerine detonated in the container, which breaks at a pressure of about 200 at, the gelatinized nitroglycerine (93:7) did not provide detonation even with its ignition in the container, which is broken at 1200 at.

In experiments on combustion under constant pressure nitroglycol, gelatinized by 3% collodion, burned evenly and stably, as we have seen, in the whole studied interval of pressures -- up to 150 at, while the liquid nitroglycol indicated the disturbance of the uniformity of combustion at a pressure 10 times lower.

The theoretical analysis of the stabilizing effect of viscosity on the basis of the same considerations which were followed by Landau,

¹If a tube with a liquid explosive is in a state of weightlessness, then in accordance with the formula of Landau normal combustion should be unstable at any pressure. On the other hand, if imparted to a tube with burning liquid is acceleration (in an axial direction) considerably exceeding the acceleration of gravity, then, according to the remarks of Yu. B. Khariton, the stability of the combustion will increase. At an acceleration equal to 100 g, the critical rate will be 3.2 times higher.

led Levich [246] to the following expression for the maximum rate of the normal combustion of a liquid depending on viscosity:

$$u_m = (3 \sqrt[3]{\eta \rho_r^{3/2} \delta_m^{1/2}})^{1/2}, \quad (5.11)$$

where u_m — the mass rate of combustion; η — viscosity; ρ_r — density of gas products of combustion; δ_m — the density of the liquid.

Of the four greatly studied liquid nitroesters most viscous is nitroglycerine; its viscosity is 0.36 poise. The calculation gives when $\rho_r = 1.72 \times 10^{-4} \text{ g/cm}^3$ and $\delta_m = 1.6 \text{ g/cm}^2$ a maximum value of the rate — $0.17 \text{ g/cm}^2\text{s}$; the actual value of the rate is equal to $0.23 \text{ g/cm}^2\text{s}$. Thus, the viscosity of nitroglycerine is inadequate for the stabilization of its combustion.

If we accept the same values of ρ_r and δ_m , then for the possibility of the stable combustion of a liquid because of the viscosity, the latter should have had the value equal to or exceeding one poise. Experiments were conducted on nitroglycerine, the viscosity of which was increased by dissolving collodion. The fact that the capacity of the gelatin to burn stably is determined by the increased viscosity indicates the comparison of the mixture of nitroglycerine with collodion (1%) prior to gelatinization, when its viscosity is practically equal to the viscosity of nitroglycerine, and after gelatinization (viscosity, 3.5 poise). The first mixture did not burn, and the second burned stably at a rate of $0.24 \text{ g/cm}^2\text{s}$. With such viscosity the permissible maximum rate according to the calculation is $0.37 \text{ g/cm}^2\text{s}$. Nitroglycerine with an addition of 1% monomer of methyl methacrylate does not burn, and the addition of the same quantity of polymeric compound of methyl methacrylate, which sharply increases the viscosity of nitroglycerine, leads, in accordance with the theory, to stable combustion.

According to equation (5.11) the maximum rate of combustion depends, and moreover, in the same way as it follows from the equation of Landau (5.3), upon the pressure under which combustion occurs. The rate of combustion increases in proportion to the first

power or pressure, and the right-hand side of equality (in terms of ρ_T) is proportional to pressure to the $1/2$ power. Thus, the left side increases more rapidly than the right-hand side, and at a certain pressure the rate of combustions starts to exceed the value permissible by theory.

Similar to pressure, an increase in the temperature decreases the stability of combustion. The rate of combustion increases with an increase in temperature, and its maximum value decreases as a result of a decrease in viscosity.

For an experimental check of the effect of pressure, experiments were conducted with gelatin (99:1) at various pressures. At 800 mm combustion occurred evenly at the rate of $0.27 \text{ g/cm}^2\text{s}$; at the given viscosity of the gelatin the permissible rate of a combustion is equal $0.38 \text{ g/cm}^2\text{s}$. At 1000 mm combustion occurred in a pulsating mode at the rate of about $0.59 \text{ g/cm}^2\text{s}$; this rate would be stable at a viscosity of 5.4 poise, i.e., 2.5 times larger than the gelatin had.

Thus, the effect of the pressure is the same as the theory specifies. The effect of temperature on gelatins could not be verified because, as the experiments indicated, upon heating the viscosity of the gelatin does not remain constant but changes depending on the duration of the heating.

The disturbance of the normal mode of combustion and its stabilization by an increase in viscosity were not observed only for individual liquid substances, specifically, nitrates of alcohol. Whittaker and others [233] describe this phenomenon for many two- and multicomponent solutions of fuel (2-nitropropane, nitrile of sebacic acid) in oxidizers (nitric acid, nitrogen tetroxide) and connect it with an increase with the vaporization of the burning liquid of its droplets by the outflowing vapor. These investigators studied the effect of viscosity, elasticity of fuel vapors, and diameter and shape of the tube. The increase in viscosity, which was reached by the dissolution polymethylmetacrylate, decreased the rate of the combustion, which approached a certain limit, and increased the

pressure of the transition into a turbulent mode. This pressure somewhat decreases with an increase in diameter of the tube. At 14.6 at a mixture of 2-nitropropane with 97% a nitric acid burned at the rate of 0.114 cm/s; at a content in this mixture of 0.1, 0.5 and 0.75% polymethylmetacrylate the rate of combustion was equal to 0.079, 0.076 and 0.074 cm/s, and the critical pressure of the transition of combustion into a turbulent mode of the liquid and gelatinized mixtures of nitropropane and nitric acid was 76, 83, 117 and 130 at, respectively.

Experiments with gelatinized liquids allowed explaining also the question about whether or not the appearance of the pulsation of combustion is caused by a secondary flame. With the combustion of the gelatin this flame appears at the same pressure and is located even somewhat nearer to the surface than during the combustion of the liquid; at the same time the pulsating combustion is observed in the first case and is absent in the second case even when the secondary flame is located very near the surface of the burning substance. The absence of a direct connection between the appearance of the secondary flame and the transition of combustion into a turbulent mode is confirmed also by the fact that for some liquids, for example, for nitroglycerine, this transition occurs at such low pressures when still there is not a secondary flame.

As was noted above, to provide stability of combustion even at atmospheric pressure, considerable viscosity, of the order of 1 poise is required; with an elevation in pressure the magnitude of viscosity necessary for stabilization rapidly increases; for example, at a pressure of 100 at it is 1000 times more than that at atmospheric pressure.

All the experiments described were conducted at constant pressures, and experiments with increasing pressure, predominantly in steel containers, were conducted also (see page 194).

Nitroglycol, nitroglycerine, trotyl and its solutions in nitric acid were studied.

Nitroglycol easily gives the transition of combustion into detonation. Only in experiments with a disc, which withstands a pressure of 65 at, in one of two experiments the disc was forced out without damage to the tube. In another experiment with a disc forced out by a pressure of 200 at and more, detonation (a charge of 50 g) was observed. It is interesting that in experiments with the strongest disc the crushing of the tube in two of three experiments was noticeably less than that in experiments with disc of the usual strength.

Nitroglycerine under these conditions (200 at) indicates moderate crushing, and at 65 at in both experiments the disc was forced out without damage to the tube. The increase in the charge of nitroglycerine up to 200 g did not change the amount of crushing of the tube, despite the application of a stronger disc (500-700 at).

For liquid trotyl (200 g) at 100°C only combustion at maximum strength of the tube is observed. A completely different picture is indicated with trotyl in a form dissolved in nitric acid. A solution with a nitric acid content of 40% detonates with the disc, which is forced out under a pressure of 500-700 at; even at 200 at an explosion with considerable crushing of the tube is observed.

Liquids in a gelatinized were also studied. Gelatinized nitroglycerine (93:7) in the amount of 50-200 g was ignited in a tube enclosed by discs, withstanding 200 and 500-700 at (density of loading, 0.4-1.2 g/cm³) and even in the housing of a missile, which withstands 1200 at. In not one of these experiments did detonation appear.

A similar but somewhat more active behavior was indicated by 62% gelatin dynamite on the basis of sodium nitrate. With 200-gram charges only the bottom part of the tube underwent a certain crushing.

Experiments were conducted also on nitroglycerine, immobilized not by the dissolution in it of nitrocellulose but by means of the addition of an inert powder (fine-grained kieselguhr) in the amount of 1/3 of the nitroglycerine; in this case the mixture of a pasty consistency is obtained. Such a mixture behaves similar to a gelatin,

not providing the transition of combustion into detonation even if the disc was expelled under a pressure of 500-700 at. A test of mixture of nitroglycerine similar in the physical structure with fine powder hexogen did not give that effect which was observed with the mixture with the kieselguhr.

In summarizing the results of the experimental check of the theory of the stability of combustion of liquid explosive, one should state that all the obtained results with respect to the effect on this stability of physical characteristics of the liquid and the conditions of combustion agree well with predictions of the theory.

CHAPTER VI

FLASH AND COMBUSTIBILITY OF EXPLOSIVES

I. Flash of Explosives

1. Mechanism of Formation of a Flash

If an explosive is heated by an external source of heat, the initial temperature of which is relatively low and gradually increases, then upon the reaching of its certain value a spontaneous combustion (flash) explosive is observed. Values of the temperature of the flash for a number of explosives under certain standard conditions of determination are given in Tables 43 and 44.

Somewhat more laborious but physically simpler is the determination of the flash point by means of heating of the explosive at a constant temperature of the source of heat. It establishes, other conditions being equal, the minimum temperature of this source beginning from which the given substance provides a flash. Another characteristic of the phenomenon is the delay of the flash — the time from the beginning of heating to its formation. Sometimes the temperature at which the flash occurs with a definite delay, for example, not more than 5 s, is determined.

Table 43. The flash point of various explosives according to Kaste
 [Translator's Note: this name is not verified].

Explosive	Flash point °C	Explosive	Flash point °C
Nitroglycerine.....	200-205	Hexanitrodiphenylamine	248-252
Nitroglycol.....	195-200	Tetryl.....	190-194
Pyroxylin.....	195-200	Hexogen.....	230
Collodion cotton.....	204-205	Cheddite (type 60).....	258-265
Pentaerythritetetranitrate	205-215	Ammonite.....	Do not provide flash or flash above 300°
Fulminating gelatin.....	202-208	Black powder.....	310-315
Gelation dynamite.....	180-190	Mercury fulminate.....	169-175
Dinitrobenzene.....	No flash	Lead of azide.....	305-320
Trinitrobenzene.....	The same	Lead trinitroresorcinate...	275
Trinitrotoluene.....	295-300	Lead picrate.....	285-287
Trinitrochlorbenzene.....	395-397	Lead trinitrokrezilat.....	255-257
Picric acid.....	300-310		
Trinitrocresylate.....	270-276		
Trinitroanisoie.....	290-296		

Note: The flash point was determined with the heating of a test tube with a charge of explosive in a liquid bath (at a definite - 20 deg/min - rate).

Table 44. Flash point of various explosives.

Explosive	Flash Point °C	Explosive	Flash Point °C
Glycoldinitrate.....	257	Trinitrotoluene.....	475
Diehylene glycol dinitrate.....	237	Picric acid.....	322
Nitroglycerine.....	222	Ammonium picrate....	318
Erythritetetranitrate.	225	Tetryl.....	257
PETN.....	225	Hexyl.....	325
Dipentaerythritehexa-nitrate.....	255	Mercury.....	210
Mannitehexanitrate....	205	Silver fulminate....	170
Nitrocellulose (13.3% N).....	230	Crystal azide lead..	345
Ethylenedinitramine...	190	Diazodinitrophenol..	180
Nitroguanidine.....	275	Lead trinitroresorcinate	265
Hexogen.....	260	Lead dinitroresorcinate.	265
Octogen.....	335	Tetrazene.....	154
Trinitrobenzene.....	550	Hexametylenetriper-oxidediamine.....	<149

Note: Placed into a bath with Wood's alloy is 0.02 g of an explosive in a copper case. The temperature at which the flash occurs in 5 seconds is established.

From the viewpoint of thermal effect, the essence of the phenomenon consists in the following schematically. At low temperatures the rate of exothermic dissociation of the explosive, and, consequently, the increase in heat are small and increase with temperature more slowly than the rate of the heat removal; All the heat being liberated is drawn off into the environment - between the heat

arrival and heat removal stable equilibrium exists.

At higher temperatures the rate of reaction and heat arrival increase with temperature more rapidly than the heat removal. The temperature of spontaneous combustion is that minimum temperature beginning with which the equilibrium between arrival heat and heat removal becomes unstable: the heat arrival starts to increase more rapidly than the heat withdrawal, and the rate of reaction rapidly increases and approaches spontaneous combustion.

Since the quantity of the heat being liberated is proportional to the volume of the explosive, and the heat removal (with convective heat exchange) - to its surface, then the temperature of spontaneous combustion depends on the quantity of the explosive. The more this quantity, the less (at the given form of the charge) the ratio of the surface to the volume, the lower the temperature of spontaneous combustion. Hence it is clear that the flash point is not an absolute constant of the explosive; at large sizes of the charge the flash of the given explosive can occur at much lower temperatures than are shown in the tables. Its delay can be in this case, also very great.

Conditions of heat removal are changed relatively little during the transition from one explosive to another; the same thing refers to heat which is liberated in the decomposition of a unit of weight of explosive. Therefore, the main parameter determining the flash point is the rate of caloric dissociation of the explosive. Therefore, from the flash point it is possible to judge approximately the magnitude of this rate at high temperatures. It follows to call that the rate of dissociation of the explosive can greatly depend on the conditions under which it occurs, and frequently more complexly depends on the temperature than that which results from the equation of Arrhenius. Therefore, an estimate according to the flash point of the rate of dissociation of the explosive at low temperatures can only be especially approximate and arbitrary.

The flash is a very complex process. In a number of works

[247-249] it has been shown that under equal conditions of the heat removal of the temperature of spontaneous combustion can be changed, for example, depending on the rate heating as a result of the chemical (autocatalytic or other) self-acceleration of the reaction. The time of interval between the moment of heating (constant ambient temperature) and the moment of spontaneous combustion can be very great, incomparably more than the possible time of the development of a purely thermal process, which with obviousness indicates the great role of the chemical development of the process with the formation of spontaneous combustion. As a result of the development of this process, the rate of the reaction increases, despite the fact that the temperature remains constant. When the rate of the reaction attains the value at which the heat arrival becomes more and increases with the temperature more rapidly than the heat withdrawal, spontaneous combustion appears.

Interesting investigations on the clarification of the mechanism of the flash and the role of individual factors in its combustion were conducted by Gol'binder [250]. Experiments were produced with mixtures of a tetranitromethane or nitric acid with various fuels. The mixtures of tetranitromethane with aniline are ignited at room temperature with considerable delay¹ (tens of seconds), which allows obtaining with mixing homogenous mixtures. A flash appears only if the quantity of the mixture exceeds a definite limit. However, this effect is not exhausted in this case by the change in the relationship of heat arrival and heat removal known from the theory of thermal spontaneous combustion. If a mixture is prepared in a glass container located in air, and in a steel one of the same size, placed into water, then, despite the various conditions of heat removal, the minimum quantities of the mixture and induction periods prove to be identical. In experiments with containers of different form (Fig. 245), other conditions being equal, under container a the minimum quantity of the mixture necessary for spontaneous combustion proves to be 2-4 times less than that in container b, although conditions of heat removal are completely similar.

¹Other amines (toluidine, xylidine and a triethylamine) give considerably smaller delay.

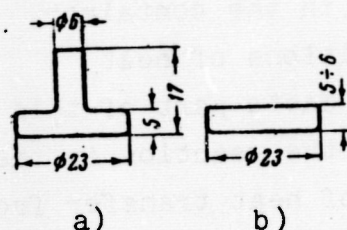


Fig. 245. Glass containers for experiments on the spontaneous combustion of a mixture of tetranitromethane and of aniline. a) semiclosed; b) open.

The measurement of the temperature in the liquid and over it indicated that during the whole induction period the temperature of the liquid remains constant and equal to the initial temperature of the components of the mixture. This also indicates that the reason for the spontaneous combustion cannot be considered as the thermal self-acceleration of the process in the condensed phase. Practically a cold mixture is ignited and then burns. Over the liquid before the combustion there occurs a rapid (hundreds of degrees per second) rise in temperature. Spontaneous combustion is preceded by "boiling," during which gases being liberated entrain the smallest drops of the liquid, forming "smoke" of their kind. One should assume that the basic process in the induction period is the thermonutral or slightly exothermic reaction of amine with an oxidizer, leading to the formation of a condensed relatively stable intermediate product.¹ Further stages of process proceed at a rate sufficient for a spontaneous combustion only when the concentration of this product attains a certain limit.

These processes consist in the formation during the interaction of an intermediate product with tetranitromethane of gases of high reaction ability, which, having accumulated in a sufficient concentration over the liquid, self-ignite. Simultaneously with the release of gases, their dilution by the surrounding air occurs. The thicker the layer of the liquid, the greater the quantity of gases is liberated per unit of its surface. This explains the effect of the quantity of the liquid on the formation of self-combustion. Easier formation of a flash in a container a is explained by the great quantity of gases

¹In accordance with this assumption, with the obtaining of the mixture in two methods the delay of the formation decreases with the increase in the time of the exposure of the first portion of the mixture.

which are liberated in it per unit volume of air in the container. The independence of the induction period of conditions of heat removal also agrees with the conclusion that the basic part of this period constitutes the isothermal development of the reaction in the condensed phase; besides this, the coefficient of heat transfer from the gas into the surrounding medium is changed during the transition from a glass container to a steel one is much less than that from the liquid.

Mixtures of tetranitromethane with fuel, being ignited only with heating up to increased temperatures were also studied. The temperature of the beginning of boiling of these mixtures was lower than the temperature of their flash. Because of this in small charges they provided a flash only at a relatively high ($>160^{\circ}$) temperature. With an increase in the charge the temperature of the flash is noticeably lowered. Thus, the mixture of tetranitromethane and benzene in the quantity of 0.1 ml flashes only at the temperature of the calorstat $\sim 500^{\circ}\text{C}$ with a small delay. If we take 25 mm of a mixture, then after heating at 130° for 3-5 min there appears a flash, which in the majority of experiments finishes with an explosion. A mixture of tetranitromethane with a "benzene low-boiling fraction" (light fraction of the pyrolysis of oil), taken in an amount of 0.05 ml, will be ignited at 190° , at 1 ml combustion occurs at $40-45^{\circ}\text{C}$, and at 20 ml it is observed at $15-18^{\circ}\text{C}$.

Very interesting data were received with the benzene mixtures, to which a small quantity of styrene was added. The presence of a total of 0.7-1.0% styrene lowered the temperature of the flash by approximately 200°C .

Mixtures on the basis of nitric acid behaved somewhat differently than did the tetranitromethane. Reactions in the condensed phase in this case are exothermic, and the temperature of the liquid rapidly rises up to a certain constant value for the given mixture, which corresponds to the boiling point and limited by it ($80-130^{\circ}$ for different mixtures). The great rise in the temperature, which leads to spontaneous combustion, occurs in the gas phase containing not

only reactive gases but also vapors or products of their thermal dissociation; furthermore, unlike the previous case, not a cold but a heated liquid burns.

Distinct from the majority of the explosives, for which the role of the chemical self-acceleration of conversion with the formation of the flash is great, is, according to experiments of Apin [251], liquid nitrogen chloride. In a soldered ampule with a load of 0.1 g at 55° it does not give a flash; at 60° always and, moreover, almost instantly there appears a flash in the form of an explosion. Apparently, such a sharp transition from a slow decomposition to an explosive one with the increase in temperature should be explained by the purely thermal nature of spontaneous combustion.

The other explosives studied can be heated to a comparatively high temperature, at which the initial rate of decomposition is relatively low and thermal equilibrium is not disrupted; only with the subsequent development of the acceleration of the reaction is there attained that critical rate, at which a heat arrival exceeds the heat removal. If with the decomposition of the substance of acceleration reaction does not occur (for nitrogen chloride this was indicated by Van't Hoff), then, obviously, the temperature limit of the disturbance of thermal equilibrium should be very sharp; the formation of the flash can only to a very small degree depend on time, which is also observed for nitrogen chloride.

On the other hand, the more self-acceleration is expressed, the wider interval of temperature - from the minimum flash point to that temperature at which the magnitude of the delay is determined only by the time of the heating of the explosive. Correspondingly, within much greater limits, the magnitude of the delay of the flash is changed. These characteristics of the phenomenon of the flash can be used for the rapid establishment of the kinetic type of thermal dissociation of the explosive.

The delay of the flash τ decreases with an increase in temperature. In many cases the dependence between them is represented in coordinates

$\lg \tau - \frac{1}{T}$ by a straight line. Such a dependence is obtained also theoretically for thermal, chain, topochemical and autocatalytic accelerations of the reaction [252]. However, the slope of the straight line, which expresses the connection of the delay of the flash and reverse absolute temperature, depends on the magnitude and form of the charge, conditions of heat exchange and other characteristics of the experiment. Therefore, the dependence between the kinetic characteristics of reactions leading to a flash and the delay of it is more complex than the indicated theories give, and it is impossible to identify the slope of straight line $\lg \tau - \frac{1}{T}$ with the energy of activation of the chemical conversion, which leads to a flash.

2. The Nature of the Flash

The temperature of the spontaneous combustion is only one of the characteristics of the phenomenon of the flash. A substantial role is played by the nature of the flash, i.e., the nature of the phenomena following after spontaneous combustion. An experiment indicates that the priming explosives and also some secondary explosives, for example, nitroglycerine and nitromannite, give a flash in the form of an explosion, and the majority of the others gives a mild flash in the form of a more or less violent combustion.

Different explanations were given by those difference. Thus, Belyayev proposed [253] that the nature of the flash is determined by relationship between the boiling point of the explosive and the temperature of its flash. If the boiling point is much higher, than the flash point, then the flash has the nature of an explosion and vice versa. However, in the comparison of boiling points, the flash points and nature of the latter for a large number of explosives, and also the effect on the nature of the flash of pressure, this assumption was not confirmed [254].

The actual reason for distinctions in the intensity of the flash can be established on the basis of the following considerations [255].

A flash can be examined simply as the combustion of an explosive. The distinction from the usual conditions of combustion consists in the following. In the first place, during the flash an explosive burns at the maximally high temperature to which it can be heated. In the second place, an explosive in the initial form does not burn, but one which is a melted (if the temperature of fusion is lower than the temperature of the flash), partially decomposed substance containing finite and intermediate products of dissociation and with changing physical features (decrease in viscosity, transition into a foamy state, in the state of boiling, etc.). Thirdly, combustion appears not from external ignition but as a result of spontaneous ignition.

The nature of phenomena following after a spontaneous ignition should be determined by whether or not combustion under these conditions is stable. In a positive case we will obtain a mild flash, and in a negative one the transition of an initiated combustion into an explosion can be observed.

One should show that judgment on the nature of the flash, specifically about its intensity, until recently had a very subjective nature; it was estimated by hearing of a sound, by the presence of the crushing of a glass test glass, etc. It was advisable to have a more objective estimate of this side of the flash. Devoted to this problem was the work of Kondrikov [256], who studied the intensity of the flash of various explosives. The measure of the latter was the height or energy of the jump of the ball lying on the opening of the test tube, placed into the thermostat of constant temperature, in which a small charge of explosive flashed.

Basic features of the phenomena are the following. At moderately increased temperatures the explosive decomposes quietly without the appearance of a flame, and the ball remains motionless. Upon reaching a certain minimum for the given conditions of the temperature there is a flash, which usually is accompanied by a flame and which forces the ball upward to a certain height. According to the nature of the change in this height with the change in temperature and other conditions of the experiment, and also according to the maximum height

of the jump of the ball at the given charge, the different explosives are distinguished from each other very substantially.

Figure 246 shows the dependence of the intensity of the flash upon temperature for mercury fulminate, typical for other studied quick-burning explosives (picrates of lead, sodium and potassium, tetrazene, lead and potassium stidnates, potassium hexylate). After a more or the less short section of the initial increase the intensity of the flash at all temperatures up to very high ones remains practically constant. The change in the sizes of the particles of mercury fulminate is not reflected in the intensity of the flash. If we use mercury fulminate not in the form of a powder but in the form of a pressed pellet, then the curve of intensity of the flash – the temperature is a maximum whose magnitude is 3-4 times less than that for powder. With the ignition of a cold pellet in a test tube the ball remains motionless; with ignition in similar conditions of the powder the ball jumps up but at a height 2-3 times less than that during the flash.

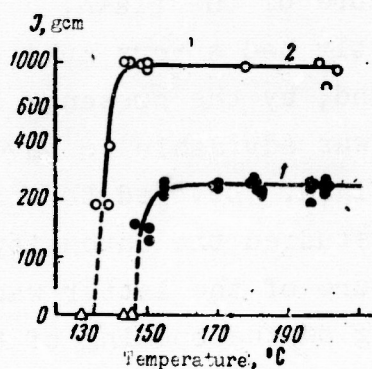


Fig. 246. Dependence of intensity of the flash of fulminate mercury upon temperature. Charges: 1 – 0.02 g; 2 – 0.05 g, Δ – absence of combustion (J – product of the weight of the ball by the height of its recoil).

The basic distinction of secondary and projectile explosives from quick-burning ones is that, starting from a certain value of temperature, the intensity of the flash falls – the height of the jump of the ball gradually decreases in most cases practically to zero.

The characteristic of trotyl is the fact that, starting from a certain rather high temperature (in the given experiments 365°C), spontaneous ignition is suddenly ceased, and the ball is forced up no more (the upper temperature limit of spontaneous ignition).

Between individual explosives known distinctions in the relationship of the increase in intensity of the flash near its minimum temperature are observed. For some of them (nitrocellulose, tetryl, dyna, the high-percentage solutions of nitrocellulose in nitroglycerine, trotyl) the increase in intensity of the flash to a maximum occurs in the considerable (sometimes tens degree of circle) interval of temperatures (Fig. 247). Other explosives (diglycoldinitrate, gelatin fulminate partly PETN), upon reaching the minimum temperature of spontaneous ignition or in the interval of 1-2°C, give a flash of maximum intensity (Fig. 248). Nitroglycerine (1 drop = 0.02 g) immediately forces the ball up to a height close to the maximum for a gelatin fulminate. However, with a further height in temperature the intensity of the flash does not fall but increases several time, and, moreover, in the part of the experiments the test tube broke into pieces; if we continue to increase the temperature, the intensity of the flash sharply drops to zero. A similar pattern of the dependence of the intensity of the flash (however, without the crushing of the test tube) upon temperature is observed for nitroglycol.

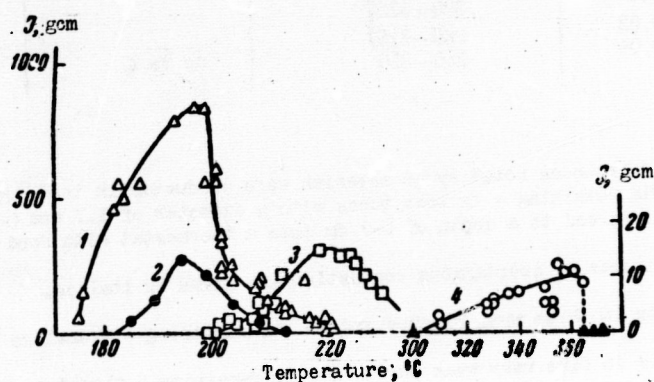


Fig. 247. The dependence of the intensity of the flash upon temperature. 1 - pyroxylin No. 1 (charge, 0.05 g); 2 - the solution (1:1) of nitrocellulose in nitroglycerine (0.02 g) - axis of ordinates from the left; 3 - tetryl (0.1 g); 4 - trotyl (0.1 g) - axis of ordinates from the right. Δ - absence (upper limit) of flash of trotyl.

Maximum intensities of the flash and some other characteristics of the experiment are given in Table 45.

Table 45. Maximum intensities of the flash of some priming and secondary explosives.*

Explosive	Charge, g	Interval of temperatures in which a flash was studied and was obtained 2° °C	Maximum intensity of the flash (J, g ² cm) 10 ⁻²	Temperature at which the burst of maximum intensity was observed °C
Mercury fulminate....	{0,02 0,05	<i>147</i> —200 <i>136</i> —200	2,5 10	155—200 145—200
Tetrazene.....	{0,01 0,02	<i>136</i> —200 142—180	0,8 2,4	140 165
Sodium picrates.....	0,02	290—335	3,1	305—335
Potassium picrate....	0,02	310—370	2,9	320
Lead of picrates....	0,02	260—300	5,6	270
Potassium hexylate..	0,02	325—375	8	345
Nitroglycerine.....	~0,02	<i>199,5</i> —320	11	225—290
Nitroglycol*.....	~0,05	<i>202,5</i> —308	8	215—270
Methyl nitrate*.....	~0,02	<i>267</i> —270	8,1	
Diglycoledinitrate*..	0,05	<i>200,5</i> —242	0,7	200
PETN.....	{0,05 0,3	<i>204</i> —276 <i>199</i> —248	1 1,6	206 202
Dyna*.....	{0,05 0,2	<i>209</i> —243 <i>202</i> —320	1 0,5	250 230
Gelatin fulminate (10% collodion).....	0,02	<i>195</i> —235	2,8	195
Powdery pyroxylin....	0,05	<i>176</i> —225	8	195
Pyroxylin powder....	0,1	<i>170</i> —205		
Tetryl.....	0,1	<i>202</i> —265		225
Trotyl.....	0,1	<i>309</i> —365		365
Hexogen.....	0,1	<i>230</i> —305		
Octogen.....	0,1	<i>285</i> —330	0—0,2	
Hexyl.....	0,1	<i>250</i> —365		
Geksanitrodiphenylsulfide.....	0,1	<i>280</i> —410		
Picric acid3*.....	0,1	<i>300</i> —325		
Amonium picrate4*....	0,02	<i>260</i> —325		
Styphnic acid.....	~0,04	<i>280</i> —320	up to 4	

*Experiments on the substances noted by an asterisk were conducted in test tubes with a diameter of 2 and height of 20 cm and the remaining - in test tubes with a diameter of 1.7 and height of 15 cm (the lower part of the test tube is immersed to a depth of 5-7 cm into a thermostat with Wood's alloy).

2*The critical temperatures of spontaneous combustion are given in italics.

3*Of the 26 experiments in three weak flashes and in the remaining - flameless decomposition were observed.

4*Of the 15 experiments in five very weak bursts and in remaining - flameless decomposition were observed.

Of studied explosives the greatest intensity of the flash is shown by nitroesters - nitroglycerine, methyl nitrate, nitrocellulose, nitroglycol, and the least - nitramines and the aromatic nitrocompounds, especially hexyl, hexsanitrodiphenylsulfide, hexogen, and trotyl, the energy of jumping of the ball for which does not exceed several percent of that which nitroglycerine gives. From aromatic nitrocompounds there is isolated styphnic acid, and in charges of

0.04 g it forces up, although completely irregular, the ball almost as high as does nitroglycol.

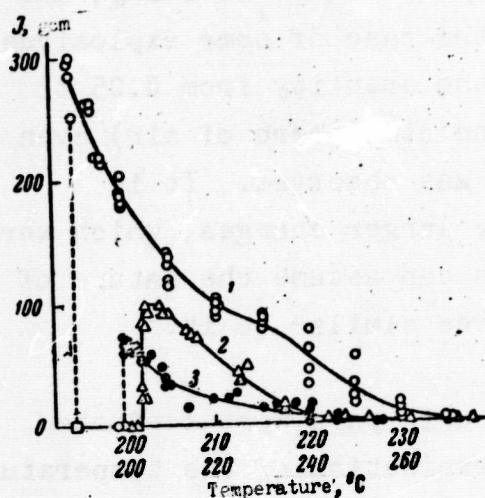


Fig. 248. Dependence of the intensity of the flash upon temperature. 1 - gelatin fulminate (10% collo-dion), a charge of 0.02 g (axis of the abscissas - upper series of numbers); 2 - PETN (0.05 g); 3 - diglycoldinitrate (0.05 g) (axis of the abscissas - lower series of numbers).

Quick-burning explosives are distinguished from each other in intensity of the flash less than secondary, and for not one of them does it reach the maximum value observable for nitroglycerine.

With an increase in the charge of the substance the maximum intensity of the burst of the majority of the explosives studied can greatly increase, in the limit - up to the formation of an explosion. However, the nature of the dependence of the intensity of the flash upon the magnitude of the charge for different explosives is different. For priming and quick-burning explosives, nitroglycerine, nitro-cellulose, and gelatin fulminate, the intensity of the flash with an increase in the charge progressively increases. Already with charges in tenths of a gram, its measurement according to the accepted method becomes impossible - an explosion occurs, which crushes the test tubes into pieces. For diglycoldinitrate, PETN and some powdery explosive mixtures (for example, a mixture of 95% ammonium perchlorate and 5% aluminium powder) the change in the intensity of the flash occurs differently: in the beginning with an increase in the charge (for PETN, for example, from 0.05 to 0.3 g) the intensity barely changes; however, when the magnitude of the charge reaches a certain critical value, the flash assumes, without any apparent section of the increase in an intensity, the nature of a powerful explosion.

Such an explosion is caused, for example, by 2 g of diglycoldinitrate. In this case in the beginning there is observed a latent combustion of the moderately boiling liquid, the rate of the combustion and intensity of boiling increase, then the whole liquid is foamy, and there follows a powerful explosion. In the case of some explosives, for example, dyna, with the increase in the quantity from 0.05 to 0.2 g (the experiment was conducted in the atmosphere of air) even a decrease in the intensity of the flash was observed. It is possible, however, that with considerably larger charges, which were not used in the given experiments a flash can assume the nature of an explosion even for a dyna and explosives similar to it.¹

The described experiments in their basic part were conducted according to the procedure usual for determination of the temperature of the flash: a test tube is located in a thermostat and put into it is an explosive.² In the study on the burst of nitroglycerine and other explosives, another procedure was used also [257]. Put into a glass flat-bottomed test tube with a diameter of about 4 mm and height 15 mm was an explosive. In the lower part at a certain height the test tube was wound by a heating wire. Experiments with nitroglycerine were conducted at a different height of the charge: 5, 3, 2 and 1 mm. At 5 and 3 mm after a short time with turbulent "boiling," proceeding with the liberation of brown nitric of oxides, an explosion occurred orderly, which crushed the test tube into small pieces, which broke the spiral and left an impression on the lead plate on which the test tube was put. This explosion is intensive enough in order to excite the explosion of the cold column of nitroglycerine, which is located in the small tube below the zone of heating. With a decrease in the height of the column of nitroglycerine down to 2 mm the test tube is crushed, but more slightly at 1 mm it remains as a whole.

¹Somewhat later it was established that with the increase in the charge to 5 g the flash of the dyna can actually assume the nature of an explosion (Editor's remarks).

²In some experiments a cold test tube of an explosive was put into a thermostat.

If the heating spiral is placed on the test tube with a considerable quantity of nitroglycerine so that its lower part would be at the level of the surface of the fluid, then the heating of the spiral leads initially to a flash with the partial burning of the nitroglycerine.

It is possible to excite an explosion of nitroglycerine not only by an external heating, but also putting a heating spiral inside the liquid; it is must, however, be located at a certain depth (1.5-2 mm). An explosion with heating on the outside could be obtained for nitroglycol; for this, however, it was required to conduct an experiment at increased pressures; at 10 at explosions were regularly obtained. On the other hand, if in experiments with nitroglycerine the pressure is lowered to 40-50 mm Hg, then its flash assumes a mild nature. This, however, refers only to experiments in a short (15 mm) test tube. The increase in its height to 40 mm leads to an explosion. The same is observed for the nitroglycol: at atmospheric pressure in 15-mm test tube a mild burst is obtained, and in a 40-mm tube an explosion occurs.

An increase in the length of the test tube, apparently, leads to an increase in pressure which appears during the flash. If suspended matter of the explosive being formed with the combustion must accomplish a longer path in the test tube, then combustion of the droplets is continued, and the pressure increases to a magnitude sufficient for the formation of an explosion; in a short test tube the suspension rapidly falls into the air, and the heights in pressure do not occur.¹

The nature of the phenomenon affect also the intensity of the heating. If it is carried out very rapidly, then a large part of the nitroglycol simply boils out of the test tube. If the heating is conducted more slowly and the liquid manages to be heated thoroughly,

¹With the combustion of nitroglycerine in the small tube, the length of which was equal to the height of the column of liquid (5 mm), an explosion with external heating (with atmospheric pressure), as a rule, did not occur.

then an explosion appears; if the heating is still weak then decomposition occurs with a weak flash or even without it. This effect of the speed of heating, apparently, is conditioned, on the one hand, by the effect of the initial temperature on the rate of combustion (and through it and on the entering of turbulization), on the other hand, it determines the volume of the liquid included by thermal decomposition and also the development of the latter.

The effect of the gas phase over the explosive in a test tube on the nature and the intensity of the flash was studied [256]. The replacement of air by carbonic acid (experiments were conducted with diglycoldinitrate, nitroglycol, methyl nitrate and nitrocellulose) substantially decreases the intensity of the flash and also increases the critical temperature and delay of the flash. In the case of nitroglycerine, during the transition from air to carbonic acid the intensity of the flash at low temperatures substantially decreases and at high - it barely changes. For a majority of liquid and melting explosives (especially for PETN, diglycoldinitrate, dyna, tetryl, hexogen, octogen and hexyl) before the flash foam is formed and, sometimes in considerable quantities. The height in the temperature decreases the formation of the foam. The effect of foaming on the rate of combustion of an explosive during a flash more clearly appears in experiments with large (1-2 g) charges of PETN, tetryl and dyna. At a high temperature the melts of these explosives, which were ignited from the surface, burn quietly by an even front and almost soundless. At a lower temperature all the liquids during the time of the preflame decomposition are absorbed into the voluminous loose foam, which burns very rapidly, sometimes with a powerful sound, and in the case of PETN under definite conditions in the form of an explosion.

I. V. Babyts and B. N. Kondrikov also studied the behavior during the flash of solutions of collodion in nitroglycerine. The introduction of 10% collodion very greatly lowers the intensity of the flash of nitroglycerine (Fig. 249). With an increase in the collodion content to 60% it remains approximately constant, and then again it sharply falls, at 75% practically to zero.

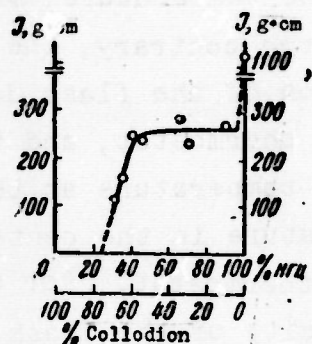


Fig. 249. Effect of the composition of the solutions of collodion in nitroglycerine on the maximum intensity of their burst (charge 0.02 g).

The intensity of the flash also depends upon the magnitude of the charge and on the temperature. Results of the study on the combined effect of these two factors are given on Fig. 250. The index of intensity of the flash was the crushing of the test tube. With an increase in the charge the temperature interval in which the flash crushes the test tube from the beginning is expanded, constituting for 1 g almost 50°, and then it becomes narrow; its right limit – in the region of high temperatures – greater than the low-temperature region, is displaced to the left; therefore with the weight of the gelatin of 10-50 g the temperature interval of the intense flash is reduced out to 10-15°C. However, under appropriate conditions this explosion is rather intensive and in experiments in a steel tube can provide its crushing similar to detonation.

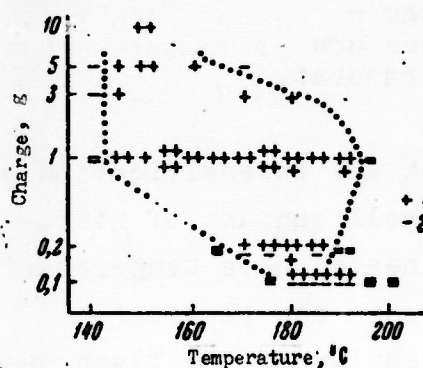


Fig. 250. Effect of the temperature and magnitude of the charge on the possibility of the formation of an explosion with spontaneous ignition of nitroglycerine gelatin. 1 - explosion; 2 - mild flash.

The measurement of temperature in the center of the spherical or cylindrical charges of gelatins indicated (Fig. 251) that at low temperatures of the thermostat heating occurs with a decreasing rate up to the achievement of the temperature of the thermostat,

whereupon there begins an accelerated height in the temperature, which finishes with a flash. At high temperatures, on the contrary, the center of the charge at the moment of the formation of the flash does not manage to be heated to the temperature of the thermostat, and the colder gelatin burns. At a definite intermediate temperature at the moment of the formation of combustion, the temperature in the center of the charge is equal to the temperature of the thermostat. For some gelatins under these conditions the maximum intensity of the flash is observed.

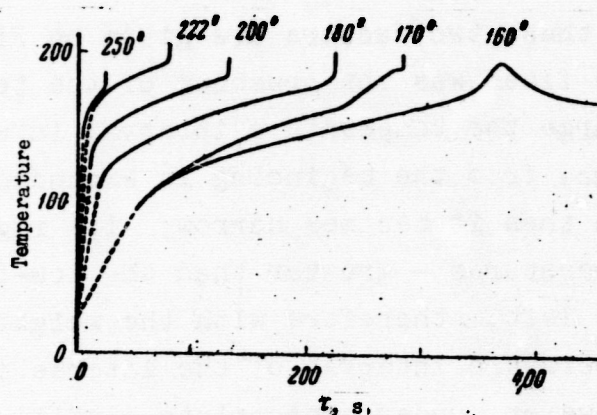


Fig. 251. Change in the temperature in the center of the spherical charge of nitroglycerine gelatin with heating (charge - 1 g). Numbers at the curves are the temperature of the thermostat.

Experiments were also conducted in which the intensification of the flash of the gelatin with a relatively small content of nitroglycerine was carried out. The gelatin was heated at a temperature below the critical and then was transferred into the thermostat and heated to a higher temperature. The intensity of the flash under these conditions can be substantially higher (Fig. 252).

Observations made during the study of the flash of nitroglycerine gelatins agree with the results obtained according to methods

described on page 356. Gelatins containing 90, 80 and 70% nitroglycerine, with a definite intensity of heating provided an explosion, which was accompanied by the crushing of the test tube, sometimes by the breaking of the heating spiral and by the formation of an impression on the lead plate. With weak heating there occurs slow decomposition, externally reminiscent of boiling. At greater heating of the gelatin up to spontaneous combustion it manages to be heated, to be diluted because of the height in the temperature and, probably, due to the depolymerization of the nitrocellulose and "to begin to boil." In these conditions the flash has the nature of an explosion. With too powerful heating of the gelatin it will be ignited on the periphery of the charge earlier than all of it will have time to be heated, then the flash has a mild nature and is accompanied by an ejection from the test tube of the greater part of the charge in a burning state. An explosion can be obtained also, although with difficulty, with smaller contents of nitroglycerine - 60, 50 and even 40%. In these cases, however, it is necessary to increase the length of the test tube and height of the column of explosive. Decomposition of the gelatins with a large content of nitrocellulose is accompanied, apart from the phenomena described, by considerable foaming.

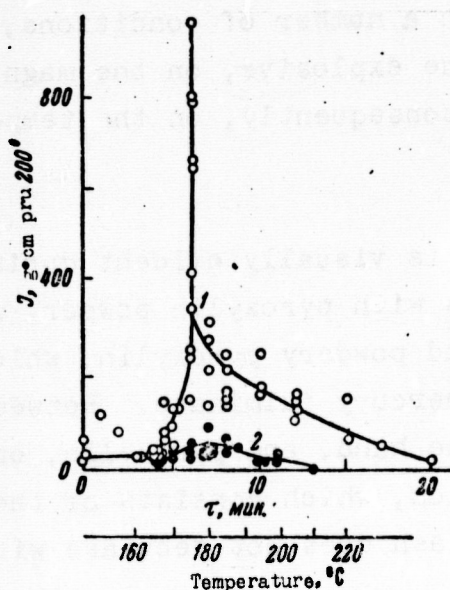


Fig. 252. Dependence of the intensity of the flash of gelatin with a relatively the small content of nitroglycerine at 200°C upon the time of its preliminary heating at 145°C (curve 1); the intensity of the flash of the same gelatin depending on the temperature during single heating (curve 2).

Observations made during the study of the flash of various explosives can be explained on the basis of the following considerations.

The absence of a flash lower than a certain critical temperature of the thermostat, naturally, is explained from the point of view of a thermal spontaneous combustion allowing for the chemical self-acceleration of the reaction with time. The effect of the gas filling the test tube indicates that a flash directly appears in the gas phase, which in this case is the mixture of vapors or volatile products of dissociation with the atmosphere of the test tube.

The intensity of the flash is determined by the rate of gasification with it, which in turn depends on the rate of combustion of the explosive. This latter depends not only upon the nature of the explosive, but also upon the mode - normal or excited - in which the combustion occurs.

With the flash of powdery explosives, one of the forms of disturbance is combustion with penetration of the process into the depth of the charge (a convective combustion) and with the flash of liquids - turbulent combustion. The transition into an excited mode is accompanied by a great increase in the rate of gasification. The possibility of the transition depends on a number of conditions, specifically, the specific surface of the explosive, on the magnitude of the normal rate of combustion, and, consequently, on the temperature at which it occurs.

The effect of the specific surface is visually evident during the comparison of results of experiments with pyroxylin powder, which generally does not force the ball up, and powdery pyroxylin, which forces it up almost as high as that of mercury fulminate. Between mercury fulminate and its analogs, on one hand, and pyroxylin, on the other, there is a considerable distinction, which consists of the fact that for it the intensity of the flash does not decrease with a

height in temperature of the experiment. Apparently, the ability to burn to the penetration into the pores of the powder of a quick-burning explosive is so great that the penetration occurs under the given conditions of the experiment independently of the temperature of the charge. In the case of pyroxylin the penetration occurs only if before the spontaneous ignition it had time to be heated. In the case of liquid (at the temperature of the flash) explosives a substantial role is played by the possibility of the formation of turbulization of the combustion. It is conditioned, first of all, by the relationship of their rate of combustion in conditions of the flash and the maximum value of the rate of normal combustion according to Landau (~ 0.25 g/cm²s at atmospheric pressure).

Table 46 gives the approximate values of the rates of combustion of a number of explosive at the flash point, which were obtained by extrapolation on the basis of data for lower temperatures, and the characteristic of the behavior of explosives during a flash. Those substances which have the rate of combustion exceeding the maximum value give an explosion with spontaneous combustion, while for substances with a mild flash the rate of combustion is much less.

Table 46. Dependence of the nature of the flash upon the magnitude of the rate of combustion of explosive.

(Weight of explosive 0.3 g).

Explosive	Flash point °C	Rate of combustion at the flash point g/cm ² s	Nature of flash
Nitroglycerine....	200	~ 0.5	Sharp sound, test tube is crushed into small pieces; Wood's alloy splashes out from bath
Nitromannite.....	180-190	~ 0.7	
Nitroglycol.....	200	0.096	Weak sound, test tube in all cases is not damaged, mild flash.
PETN.....	205	0.120	
Tetryl.....	190	0.210	
Hexogen.....	230	0.084	
Trotyl.....	300	0.040	

With the flash some additional phenomena, which affect the course of combustion are possible.

In principle that case is possible when with heating the complete thermal and chemical homogeneity of the heated substance is retained. Then the substance will by the moment of combustion be heated to a maximally high temperature, the centers of combustion will arise immediately in a very large number, and the time from the moment of spontaneous combustion to the moment of the completion of the reaction will be very little. This is the most rapid homogenous explosion of the substance.

It is obvious, however, that in real conditions of the formation of the flash with the exothermic and self-accelerating character of dissociation of the explosive, it is not possible to expect the isochronous formation of centers of combustion in its entire mass. The reaction appearing at any point induces conditions for the reaction of adjacent molecules which are more favorable than in the mass of the substance as the whole. Furthermore, the explosive at different points is found in various conditions with respect to the heat emission (and, consequently, temperature) of the concentration of products of this reaction accelerating the reaction, the contact with the air, etc. Therefore, one should assume that the beginning of the flash can be the appearance of one (the first) center of stable combustion.¹

Further occurrence of combustion depends on a number of factors, in the first place, upon the possibility or impossibility of the stable combustion of a substance heated to a given temperature and partially decomposing. If even at the moment of spontaneous combustion

¹The center of the stable combustion is understood as the origin of the combustion, which is able to spontaneously burn. Judging by some works, its formation can precede the formation of centers of the smaller sizes, not giving unlimited self-propagation of the flame.

the state of the substance allows stable combustion, then this condition will necessarily be fulfilled in the whole extent of the combustion.

A considerable role in this case is played by the mass of the explosive. If the state of the substance at the subsequent time after the formation of the center of combustion is not changed, then with a small mass the whole substance can burn from the first and only center of the combustion. With greater mass of the substance for the time of the propagation of the combustion, which was initiated from the first center of combustion, the formation of new centers, which will lead to an increase to a certain extent of the intensity of the phenomenon is possible.

This complication of the initial process is all the more probably in that usually the state of the substance does not remain invariable during the time after combustion but continues to be changed in the direction of the increase in the probability of the appearance of centers of combustion (the height in temperature as a result of external heating and a self-heating, the increase in the concentration of intermediate or end products, which accelerate the conversion).

The development of the chemical reaction of dissociation can be reflected in the change in the course of combustion even independently of the appearance of new centers of combustion. This reaction occurs as a rule, with the liberation of gases; the intense liberation of bubbles of gas, which rise upward and break through the front of the combustion, breaks this front and leads to the acceleration of the combustion, which is accompanied by the entrainment of drops of liquid into the flow of the outflowing gases. Similar consequences is seen in the formation of foam in the decomposing liquid explosive.

It follows to explain by these factors the unique nature of the combustion, which was observed with spontaneous combustion as a

result of the external heating of the charge (100 g) of picric acid in an Erlenmeyer flask with a capacity of 250 cm³. From the beginning the substance was melted, and then the formation of white vapors and their weak flash with the ignition of the liquid were observed. After 30 s foaming with the ejection of a shower of burning sprays, which was finished with a dull knock with the breaking of the flash occurred.

The same pattern is observed during the combustion of greatly heated liquid trotyl, which appears from external ignition or as a result of a spontaneous ignition. Being uniform at lower temperatures, it becomes pulsating and is accompanied, just as during the combustion of picric acid, by an ejection of burning drops of liquid.

Apart from the decomposition as a result of the spontaneous development of the reaction, under these conditions a known role at a small magnitude of the rate of the combustion of trotyl can be played also by the heating of the liquid because of the transfer of heat along walls of the vessel: at lower temperatures combustion in the beginning was uniform, but, having approached to the end of the tube, it became pulsating, since the tube stood on a base of a material poorly conducting heat, the heat had nowhere to depart, and there was great heating of the walls.

Interesting in this respect are also experiments of Gol'binder [258] on the transition of combustion into an explosion of a mixture of aniline with tetranitromethane, the mechanism of spontaneous combustion of which was described above.

The highly exothermal reaction, which leads to spontaneous combustion, appears in the gas phase or, more accurately, in the gas-vapor-drop suspended matter over the surface of the liquid. The combustion of the gases or of vapors leads to combustion of the liquid mixture.

This combustion is propagated with a considerable rate exceeding that value of it at which there usually appears autoturbulization of

the surface of the burning liquid unevenly and with a powerful pulsation. Just as for some other explosive liquids, during the transition of combustion into a turbulent mode under definite conditions the extinguishment of combustion, in this case, temporary, is observed; reactions which lead to spontaneous combustion are continued, and after extinguishment they again cause spontaneous combustion. As a result of this combustion can occur in the form of alternating flashes with a frequency greatly distinguished for different explosives.

A study of conditions of the transition of combustion into an explosion indicated that the increase in the height (and not total mass) of the column of the liquid is highly favorable to it; the critical height for mixtures on the basis of aniline and o-toluidine is about 10 cm. The length of the section burned up to the transition into an explosion does not indicate a regular dependence on the general height of the column of liquid. The height in initial pressure increases the rate of combustion and facilitates its transition into an explosion.

The transition of combustion into an explosion and the effect on it of the height of the charge is explained in the following manner. Combustion by itself occurs at a rate sufficient for its acceleration due to the formation of turbulization. This acceleration is additionally intensified by passage through the fluid of bubbles of gases, which create relief of the surface of the liquid and take away the drops of liquid into the zone of the hot products of combustion. This additional acceleration, as the experiments indicated, in this case is decisive. At the height of the charge of 10 cm in tubes with a diameter of 5 and 18 mm, combustion occurred without an explosion. In the composite tube, the lower section of which (4 cm) had a diameter of 18 mm and the upper (6 cm) - 5 mm, combustion turned orderly into an explosion. The active nature of the intermediate gas products contained in the bubbles, which are formed in the liquid, just as on the mass of the foam, the cells of which are filled by the same products

further the formation of the explosion. It is known, according to experiments of Bowden, that the presence in the liquid even of follicles of an inert gas favors it; it is obvious that with the hot gas, which has the capacity for rapid exothermal reaction, this effect of the bubbles will be even more expressed.

A gas or foam explosion, naturally, causes the explosion of a heated liquid.

A similar combustion of large quantities of explosives, especially with continuing external warmup of the vessel, which is accompanied by an ejection of sprays of the liquid into the flame, can be finished with a detonation, which was often observed with fires in the production.

Besides that shown, the quantity of the substance can have even the following effect. If the combustion is unstable and able to turn into a detonation, then at too small a quantity of the substance the explosive can burn before a detonation mode will be achieved. In experiments on an unstable combustion of powdery and also liquid explosives, the transition of the combustion into an explosion was observed only when the height of the charge exceeded a certain minimum.

In certain cases, as we have seen, taking part in the formation of a flash are vapors of the explosive or their mixture with the surrounding gas (usually air). The flash of vapors can be reflected in the whole phenomenon for two reasons. The combustion of vapors or of their mixture with the air can lead to their detonation, which in turn can cause the detonation of the heated condensed phase.

It is known that detonation of the gas with its sufficient density is able to cause detonation of the condensed explosive [259]. Besides the direct field of detonation of the heated liquid by the gas explosion, the latter can further the formation of the detonation in the following indirect way. The degree of the stability of combustion,

as we have seen, greatly depends on pressure. The height in pressure created by the gas explosion can in certain cases be sufficient to transfer the combustion into an unstable region. With the heating of the methyl nitrate in a test tube to a temperature close to the boiling point, and up to the ignition of the vapors, their detonation appeared, which led to the detonation of the liquid.

Very uniquely, not with heating but with cooling, as a result of the spontaneous combustion of vapors, the flash of liquid nitrogen chloride appears [251]. The upper end of the soldered small tube with the nitrogen chloride was at room temperature, and the lower end was immersed into a cooling mixture. When the temperature of the liquid was lowered to -25° , an explosion occurred. The mechanism of the formation of this explosion, according to Apin, is the following. For vapors of nitrogen chloride, as a result of the chain mechanism of its dissociation, there exists the upper limit of pressure, below which even at room temperature their spontaneous ignition occurs. With the cooling of the liquid nitrogen chloride, the pressure of the vapors over it is lowered, when the upper limit is reached, the vapors are ignited, causing combustion and usually an explosion of the fluid.

3. Upper Temperature Limit of the Flash

In the study of a flash the unique phenomenon called the upper limit of the flash point was detected [260]. It consists in the fact that for some volatile explosives (trotyl, picric acid, xylyl), the flash, which is observed upon the introduction of a small charge of explosives into the heated test tube, does not occur if the temperature of the test tube is higher than the defined limit; instead of a flash flameless decomposition is observed. In nitroglycerine the detonation taking place during a flash in the interval of temperatures of $200-220^{\circ}\text{C}$ alternates at a temperature above 250° with the rapid combustion without apparent sound and mechanical effects. In tetryl the upper limit of the flash point it is not observed.

The existence of the upper limit is explained by the fact that the formation of the flash depends not only upon temperature, but also on the concentration of products of dissociation, intermediate or final. Since the development of thermal dissociation, which includes a series of reactions, depends, specifically, upon the temperature, one can assume that at high temperatures of the experiment and, respectively, rapid heating of the explosive to the boiling point that high concentration of intermediate products which accelerate the conversion which is necessary for spontaneous combustion is not reached. This explanation is indirectly confirmed by experiments at which there was used trotyl partially decomposed at a low temperature and which gave a flash even at temperatures higher than the upper limit.

Processes occurring with heating under the conditions of the experiment described above must be imagined in the following manner [254]. If the temperature of the bath is low and heating occurs slowly, then at the moment of achievement of the boiling point the concentration of accelerators is sufficient for the formation of spontaneous combustion, and the latter occurs.

If the temperature of the bath is high and heating occurs rapidly, then at the moment of the achievement of the boiling point the concentration of products of the reaction will be inadequate for the initiation of spontaneous combustion, and the substance is converted into vapor. Decomposition will occur without a flash, since in a vaporous state with identical dynamic characteristics for the formation of spontaneous combustion a higher temperature is necessary: the quantity of the heat which is liberated per unit volume is considerably (200-1000 times) less (according to less density), and the thermal conductivity of the vapors is less than the thermal conductivity of the liquid by only approximately 10 times. Furthermore, the self-acceleration of the dissociation of the majority of explosives studied into vapors is less than that in a molten state.

The clear confirmation of this explanation is given by results of experiments [261] in which there was measured the change in the temperature of a small (0.1 g) charge of trotyl, which was dropped into a test tube inserted by 1/3 into heated Wood's alloy. Curve 1 (Fig. 253) shows the change in temperature of the trotyl with the temperature of the alloy of 340°C; after 19 s there was achieved a temperature 337°C, which is close to the boiling point, and a flash occurred. At the temperature of the alloy of 380°C (curve 2) this temperature was achieved in 8 s; after a certain cessation of the rise in temperature, obviously, induced by the boiling up of the trotyl, it continued to rise and was tracked up to 360°C, and flashes thus did not occur.

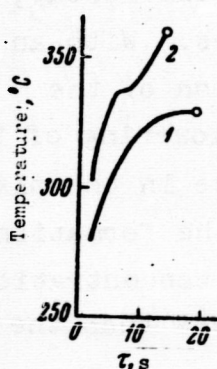


Fig. 253. Change with time of the temperature of trotyl during rapid heating. 1 - at the bath temperature of 340°C; 2 - at the bath temperature of 380°C.

The upper limit of the flash point is given by not all the explosives but only those whose boiling point is comparatively low with respect to the flash point; explosives whose boiling point is higher than the flash point (tetryl, hexogen and others), or which generally are not able to boil (pyroxylin), do not have an upper limit of the flash point.

Gol'binder [250] paid attention to the similarity of the phenomena which were observed by him with the flash of liquid mixtures, which occurs on the upper limit of the temperature of the flash of the individual explosives. The many volatile mixtures, taken in small quantities, indicate the phenomenon of the upper limit in the whole interval of temperatures from room temperature to

500°C, when it is more correct to indicate not the flash of the explosive but the combustion of its vapors by the heated surface. If we increase the thickness of the layer of the mixture, then the time of the vaporization increases, and the self-acceleration of dissociation manages to occur earlier than the whole explosive is evaporated, and therefore the upper limit is lowered.

Very clearly illustrated is the role of the chemical self-acceleration and volatility of the experiment with respect to the addition of small quantities of styrene to the mixture of benzene on a tetranitromethane, which sharply (down to 200°C) lowers the temperature of the flash. Mixture itself of benzene with tetranitromethane is chemically comparatively inert; therefore, its spontaneous combustion appears only at such a temperature of the thermostat, at which the mixture of vapors, i.e., about 500°C flashes. With an admixture of 0.5% styrene the condition of vaporization of the mixture cannot be substantially changed. The great lowering of the flash point is explained by the fact that the presence in the mixture of reactive styrene leads at a lower temperature to the formation with a sufficient rate of active products. The necessary concentration for their spontaneous combustion is induced for a time less than the time of complete vaporization.

In conclusion it should be noted that the upper limit of the flash point is not an absolute limit and only limits from below the temperature interval in which a flash is absent. At higher temperatures a flash appears again, but this, obviously, is a flash or even combustion of the vapors.

Conclusion

A flash of an explosive is the combustion of heated substance which appears by means of spontaneous combustion. This spontaneous combustion occurs as a result of self-heating of the explosive because of the exothermal and, as a rule, self-accelerating reaction of its

thermal dissociation. The minimum temperature of a flash depends on the size of the charge and duration of heating, which determines the chemical acceleration of the conversion.

The nature of the flash is determined by the stability of the combustion at the temperature of spontaneous combustion. If the combustion is stable, the flash has a mild nature, which is reminiscent of a normal combustion; if the combustion is sharply unstable, then the flash assumes the nature of an explosion, especially, if the mass of the explosive is great.

The intensity of the flash of priming and quick-burning explosives in a powdery form increases with an increase in temperature of the thermostat to a maximum, and with further height in the temperature it remains constant. For secondary explosives after a maximum there is observed a decrease in the intensity of the flash, which is connected with the fact that the combustion of the charge, which did not manage to be heated, is more stable.

If the conditions of the heating and volatility of the explosive are such that it is rapidly converted into vapor, before the decomposition occurs to a considerable degree there will accumulate a sufficient quantity of the intermediate products accelerating the conversion, and then a flash with a flame is absent. Because of this, with a height in the temperature of the heating for volatile explosives, there is observed the upper limit of a temperature, above which the flash ceases and appears again in the form of a flash or of combustion of the vapors at considerably higher temperatures.

II. Combustibility of Explosives

Combustibility is an important property of explosives, especially important in certain specific conditions of its use. These, first of all are, barrel and reactive detonation. The task of the igniter is to provide (for a possibly short time and without an excessive increase in pressure) the formation of combustion on the entire surface of the charge. The imperfections of inflammation can have, especially in reactive systems, more difficult consequences - the increase in the burning surface as a result of the penetration of combustion into cracks in a charge formed with combustion, the result of which is damage to the engine.

Combustion of an explosive can occur during explosive operations in mines; with failure of detonation or with its stopping for a certain reason the remaining part of the charge can burn if the combustibility of the explosive is great and conditions for inflammation are carried out: the effect of gaseous products of detonation are quite intense in duration and magnitude of pressure.

Finally, in many conditions of the activation of an explosion by a mechanical impulse, the first stage of the process is combustion, and its formation is determined, specifically, by the combustibility of the explosive.

Between the flash, which occurs during the slow heating of the explosive, and the combustion, which appears with its very rapid heating, there is considerable difference.

If the charge of an explosive is heated to a certain moderately increased temperature, then if this temperature is not too low, and the sizes of the charge are not too small, it gives a flash. The physical meaning of this phenomenon was examined in the previous section; the explosive is wholly heated to the temperature of the thermostat at which the developed exothermic reaction occurs. When the heat arrival due to this reaction starts to increase more rapidly

than the heat emission, there is a flash, which is the spontaneous ignition and subsequent combustion of the substance.

It is possible to calculate the minimum quantity of heat applied to the substance on the outside necessary to obtain a flash. It is equal to the product of the mass of the explosive on its heat capacity and on ΔT - the difference in the temperature of the thermostat and initial temperature of the substance. Thus, this quantity is proportional to the mass of the substance: with greater mass it will be greater.

If the same charge is affected by a source of heat of high temperature, for example, by a flame, then there will also begin combustion, but the quantity of heat necessary for the combustion will be considerably less than that in the first case, and practically will not depend on the mass.¹

Thus, although both phenomena are the combustion of the explosive caused by external heating, as a result of the distinction of temperatures of heating they are considerably distinguished from each other.

What is the mechanism of the process in the second case?

With the effect of the high temperature, for example, heated gas on the surface AB of the explosive (Fig. 254), the temperature on this surface does not reach at once its maximum value. The magnitude of the temperature of the surface layer is determined by two

¹Sometimes, in attempting to determine the delay of the flash at very high temperatures, an explosive is inserted into a greatly heated test tube. Actually under the conditions of such an experiment there will be realized not a flash but a combustion of the explosive, and, naturally, its results are similar to those which are obtained with the ignition of the explosive by the touching to it of a greatly heated rod or with an ignition by the greatly heated condensed gas, etc., i.e., to a greater or lesser extent they characterize the combustibility of the explosive.

processes: by the imparting of heat by the heated gas to the surface of the explosive and by the removal of the heat from the surface and into the depth of the substance.¹

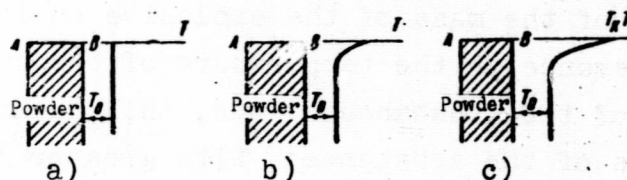


Fig. 254. Change in temperature on the surface of the explosive (powder) with combustion. a) in the beginning of heating the temperature of the surface layer is equal to T_0 ; b) in the course of heating the temperature of the surface bed is more than T_0 but less than T_K ; c) at the moment of the combustion the temperature of the surface layer is equal to T_K .

The magnitude of heat removal into the substance is determined by the difference in the temperature of the surface and temperature of the adjacent layers. In the beginning (Fig. 254a) these layers have a temperature equal to the initial temperature of the explosive (T_0). With the heating the temperature of these layers increases, and as a result of this the heat removal into the depth of the substance drops (Fig. 254b). If we consider the rate of the imparting of the heat to be constant, then a decrease in the heat removal means the rapid increase in the temperature of the surface layer. When this temperature reaches a certain limit T_K - the point boiling (Fig. 254c)

¹Here just as in the whole further investigation, it is proposed that in the condensed phase a chemical reaction does not occur. This is completely correct only for the combustion of volatile explosives at low pressures. If in the combustion there is a considerable liberation of heat in the condensed phase (or the disturbance of its physical structure, for example, dispersion with the combustion of some explosives), the stated considerations and conclusions lose, to a greater or lesser extent, their applicability.

for volatile explosives or the temperature of rapid gasification for nonvolatile explosives, then vapors or gaseous products of the initial reaction of decomposition are formed. These vapors are heated rapidly - respectively to their small volumetric heat capacity - to such a temperature at which there approaches a very rapid exothermal reaction; which leads to the final products of combustion under the given conditions. This is combustion.

If at the moment of combustion the effect of the external source of heat is ceased, then the fate of the appearing combustion can be different depending on the thickness of the heated layer formed with it of the condensed phase.

Actually, with steady combustion at a given pressure and initial temperature, the thickness of the zone of heated and the thickness of the heated layer have a quite definite magnitude. This thickness is determined by the rate of the thermal wave, which escapes into the thickness of the substance, and by the rate of the motion of the front of combustion, which overtakes and pushes this wave.

Theory [238] indicates that near the surface there is a definite distribution of the temperature in the condensed phase.

Let us assume the intensity of heating with combustion will be such that at the moment of achievement by the surface AB of temperature T_K the distribution of temperature in the heated layer of the condensed phase will correspond to that which takes place with steady combustion. In this case combustion leads to the formation of steady combustion (Fig. 255a).

If the intensity of heating is less, then at the moment of achievement by the surface of a maximum temperature T_K the thickness of the heated layer will be more than that which corresponds to steady combustion, in other words, the curve of the drop in temperature from the surface into the depth of the condensed phase will be flatter than it is in the first case (Fig. 255b). Then with a fixed increased in the heat arrival from gases of combustion the heat removal into the thickness of the substance will be less. Because of the increased

difference in the heat arrival and heat removal, the gaseous products of combustion will have a great reserve of heat, i.e., a greater final temperature. Therefore, the rate of combustion in the beginning is greater than that during steady combustion. The pattern will be the same as if in the beginning the preliminarily preheated substance burned.

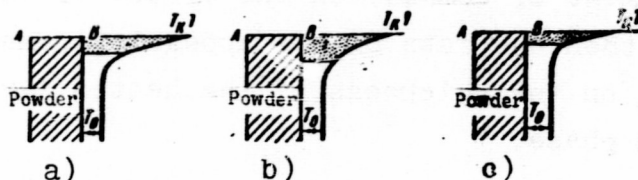


Fig. 255. Change in thickness of the heated layer with combustion depending on the intensity of heating. a) heated layer of a thickness normal for the steady combustion; b) heated layer is thicker than normal; c) heated bed is thinner than normal.

When the front of the combustion, in overtaking the departed forward thermal wave, to the cold substance, the temperature gradient near the surface will increase, the rate of combustion is decreased up to a value which corresponds to a steady-state operation, and combustion will be continued at this rate.

If a combustion occurs under conditions at which the increase in pressure because of the gases of combustion does not occur, then the only distinction of the second case from the first will consist in the more rapid combustion of the initial section.

If the intensity of heating is more than that in the first examined case, then at the moment when on surface AB a maximum temperature is achieved, the thickness of heated layer will be less than that which corresponds to steady combustion (Fig. 255c).

If the source of heat at this moment ends its action, then the temperature gradient at the surface will be more than the steady, and the heat arrival will not compensate the heat emission and the

combustion appearing can be extinguished slowly. It is understandable that if the effect of the source of heat will not be ceased then it will cancel the heat losses, and the combustion, slow in the beginning, in accelerating, will achieve a normal rate, but the heated layer, being thickened because of the slowness of combustion, will achieve its normal thickness.

Thus combustion occurs at different temperatures of the heat-transfer agent and under conditions in which a noticeable increase in pressure with combustion is absent.

For these conditions it is possible to calculate on the basis of the laws of heat transfer the time of combustion, for example, with the action by a jet of hot gas. This is the time necessary for the achievement on the surface of a definite temperature, point of boiling T_K or temperature of decomposition T_p .

In exactly the same manner it is possible to calculate also the time of the normal combustion, which leads to the formation of a heated layer with a thickness which corresponds to steady combustion; for this with calculation it is necessary that the temperature of the heat-transfer agent be taken equal to the combustion temperature.

Let us turn to the question of the connection of combustibility with characteristics of explosives and the process of combustion.

The basic question of normal combustion in the formation of the heated layer of thickness corresponding to the given conditions (p_0 and T_0). The heat reserve in this layer can be a measure of the combustibility of the substance.

If in the condensed phase, which is adjacent to the front (interface of the condensed phase and vapors or gases), there exists

a Michelson distribution of temperature,¹ then temperature T at a distance of x from the front is determined by expression (4.15) (page 268).

$$T = T_0 + (T_K - T_0)e^{-\frac{x}{\delta}}, \quad (6.1)$$

where T_K - temperature on the surface of the condensed phase, in the case of liquid volatile explosives - the boiling point, in the case of the nonvolatile explosives - a certain temperature proposed by Zel'dovich as approximately constant at which the condensed phase rapidly turns into gases.

The quantity of heat Q in the heated layer can be calculated from expression

$$Q = \int_0^{\infty} c_p \delta (T - T_0) dx = \frac{\lambda}{\alpha} (T_K - T_0). \quad (6.2)$$

This expression indicates that it is impossible, as sometimes is done, assume as the characteristic of combustibility the temperature of spontaneous combustion of an explosive. In the first place, this temperature is not constant, but depends, as we have seen, upon the duration of heating and other factors and, generally speaking, is lower than T_K . Only at very small times of delay does the temperature of spontaneous combustion approach T_K . Further Q depends not only upon T_K , but also upon the thermal conductivity of the explosives and the rate of its combustion. At the same time with respect to thermal

¹Some investigators indicated that in conformity to the practically most interesting case - the combustion of the powder - the indicated condition is impracticable on account of the fact that with heating in the condensed phase the exothermal reaction of decomposition occurs, which disrupts the Michelson distribution of temperature; in principle this observation, which is completely probable, is correct. It is possible [262], however, that the effect of the exothermal reaction will be so insignificant that it will not be reflected substantially on the possibility of the application to the given case of the theory of the heated layer in its simplest form.

conductivity and especially with respect to the rate of combustion, various explosives are substantially distinguished from each other. Therefore, two substances, which possess a similar temperature of spontaneous combustion, for example, trotyl and black powder, can have a sharply different combustibility according to a distinction of 60 times of their rates of combustion.

Belyayev [263] compared the combustibility with volatility, assuming that the more the volatility, the more combustibility. This conclusion is valid only to the extent that, other conditions being equal, the necessary heat reserve for volatile substances is more when the boiling point is the higher. However, other conditions, as a rule, are not equal; furthermore, the concept of volatility is conditional, and for nonvolatile explosives T_p can be less than the boiling point for some volatile substances.

It is impossible to consider as theoretically valid also the experimental method which was used by Belyayev for the determination of combustibility: the wire incandesced for 5 s, touched the surface of the substance; established was that temperature up to which the substance should be heated in order that the inflammation would occur. At these conditions there occurs a combustion of not the explosive as such, but of the mixture of its vapors or products of decomposition with the air, the combustibility of which cannot have anything in common with the combustibility of the explosive. Thus, the combustibility of the fuel not capable of an independent combustion can be determined.

The equation for the storage of heat gives the dependence of combustibility upon the temperature of the substance. The necessary heat reserve decreases with an increase in temperature, since the difference $T_K - T_0$ decreases and, furthermore, it increases the rate of combustion.

The dependence of combustibility upon pressure can be obtained by substituting u with the expression of its dependence on pressure.

Taking for this dependence the equation of direct proportionality $u = B \cdot p$ we have

$$Q = \frac{\lambda}{B \cdot p} (T_x - T_0). \quad (6.3)$$

i.e., the necessary heat reserve is approximately inversely proportional to the pressure.

It is known that with the escape of unburned power grains from the gun barrel with a shot their extinguishment is observed. The heat reserve in the heated layer during combustion under high pressure in a gun barrel is small and proves to be inadequate for combustion under atmospheric pressure, although the powder, ignited at this pressure, is able to burn.

With a decrease in the density of the powdery substance its combustibility increases, since the linear rate of combustion increases, and simultaneously the thermal conductivity of the powder decreases.

Experimental Determination of Combustibility of Explosives

The most widespread are two methods of experimental determination of combustibility.

Placed over the explosive at a certain height vertically a segment of Bickford fuse or an exploder. That maximum distance at which an explosive is ignited is established. This distance is taken as a measure of combustibility. Such a method, naturally, allows the giving of only a comparative estimate of combustibility.

The second method consists in the fact that the surface of the explosive is subject continuously or periodically to the effect of high temperature, for example, a gas flame. The minimum time of the effect of the source of heat, which leads to combustion, serves as a measure of combustibility. With respect to this method it must be

noted that, in the first place, there will be ignited initially not the vapors of the explosive but their mixture with products of combustion of the gas flame, and, possibly, with air. In the second place, the temperature of the heating cannot correspond to that at which at the moment of the combustion the thickness of the heated layer is equal to its thickness with steady combustion. If the temperature of combustion of the gas flame is lower than the temperature of combustion of the explosive, then results (the quantity of heat) is overstated; if the temperature is higher, then the phenomenon of steady combustion will have a more complex nature, and it will be difficult to evaluate results of the experiment.

By this method Cronquist [264] determined the combustibility of various powders. The powder grain, fixed in the lower end of the pendulum, passed with its motion through the flame. The duration of the passage of the grain in the flame up to combustion served as a measure of combustibility. The obtained times are expressed in hundreds of milliseconds and for smokeless powder somewhat less than that for different types of black powder.

If we judge by this datum, then one should conclude that the combustibility of black powder is much less than that of smokeless powder, which corresponds neither to the experience of practice nor to results of methodically correctly conducted laboratory experiments (see below). The inaccuracy of results obtained by Cronquist for black powder is explained by the fact that the intensity of heating (temperature of the flame) in his experiments was too small. Therefore, for black powder the necessary time of the heating was so great, that in fact there was determined not its combustibility, but the flash point. In order to obtain a correct concept on the combustibility of black powder, it is necessary to use a higher temperature of heating in testing.

In principle such a method of the determination of combustibility would be correct where the surface of the substance would be subjected to the action of a chemically inert heat-transfer agent with a

temperature equal to the temperature of combustion of the substance. This can be accomplished, for example, in the form the dropping of a thin plate of a substance (powder) in a vessel with heated inert gas or the products of combustion of powder. The time up to combustion and the time of combustion are recorded. At low temperatures of the gas in this case simply the flash point is determined. The higher the temperature will be the less will be the time up to combustion, and the greater the time of the combustion. That temperature of inert gas at which the time of combustion is equal to the time of the steady combustion of the plate of given thickness is the temperature of combustion of the powder, and the time up to combustion at the temperature is the measure of combustibility. Experimentally this method has not been realized.

One of the possible, theoretically valid and experimentally accomplished, methods [265] consists in the fact that placed closely on the end of the cylindrical charge of the substance, the combustibility of which must be determined, is a column of combustible substance, in the capacity of which an infusible powdery explosive, for example, pyroxylin is used. The minimum density of the igniting substance is established at which the combustion of the tested substance occurs. The less this density, the more the combustibility.

The basis of the method is the dependence of the heat reserve in the frontal layer, with which combustion occurs, upon density. From the relation $Q = \lambda/u (T_K - T_0)$ it follows that the heat reserve decreases with the decrease in density, since the linear rate of combustion increases approximately inversely proportional to the density (the mass rate is constant), and thermal conductivity decreases. Therefore, the heat reserve which transfers the igniting substance of the surface of that being ignited depends on density of the former and even can be quantitatively determined if all quantities which enter into the expression for Q are known. If this reserve is more than that necessary for the steady combustion of the tested substance, then inflammation approaches, and vice versa. With incomplete knowledge of the quantities which enter into the expression for Q ,

the minimum density of the igniting substance can serve as a comparative measure of combustibility.

A deficiency of the method is the necessity of great accuracy in the carrying out of the experiment with respect to the uniformity of density, especially as the result of the experiment is determined not by the average value of the density of the igniting charge, but by the density of the thin layer adjacent to the surface of the charge being ignited. For a more accurate determination of the maximum density, it is expedient to conduct not one, but several experiments at each density. Table 47 gives results of the experiments on the determination of the combustibility of a number of explosives according to the given method.

Table 47. Experiments on the determination of combustibility of the explosives.

Substance tested	Cubic density of tested explosives g/cm^3	Cubic density of igniting substance, g/cm^3	Results of the experiments
Nitroglycerine powder	1,58	1,08; 1,19; 1,20; 1,21 1,20; 1,21; 1,21; 1,21; 1,22; 1,28	Did not ignite Ignited
Powder VT*	0,91	0,38; 0,51; 0,54; 0,61; 0,67; 0,67; 0,70 0,62; 0,65; 0,67; 0,69; 0,70; 0,70; 0,73; 0,73; 0,74; 0,75	Did not ignite Ignited
Black powder (pulp)	1,25	0,20; 0,21; 0,21	The same
Hexogen	0,80	1,48; 1,48; 1,49; 1,52; 1,53; 1,57; 1,53; 1,55	Did not ignite Ignited
Tetryl	0,77	1,45; 1,50; 1,62	Did not ignite

Note: Used as the igniting substance in all the experiments was a mixture of pyroxylin with hexogen 80:20.

*[Translator's note: this is a transliteration from the Russian]

Results of experiments on the comparison of the igniting effect of humid and dry pyroxylin are interesting. The rate of the combustion of humid pyroxylin is considerably less, and therefore the heat reserve in the frontal layer is more. The result of this is, on one hand, lesser combustibility of the humid pyroxylin and, on the other hand higher igniting effect of it than that of the dry, despite

the fact that the temperature of the gaseous products of combustion is lower. In the experiments the density of the charge (pyroxylin) being ignited was identical (0.60 g/cm^3); the density of the igniting charge was equal to 0.20 g/cm^3 . With the igniting charge from dry pyroxylin, combustion does not occur, and humid pyroxylin (with 3.2% water) in all the experiments provided combustion.

For an estimate of the combustibility also the critical diameter of combustion, which characterizes the ability of explosives to burn (see pages 26-27 and the following). The thicker the heated layer, the more the heat losses into the environment during the combustion of the cylindrical charge. The magnitude of the rate of combustion (or pressure), the thermal conductivity of the explosive and, in the case of a powdery explosive, its density, affect the critical diameter of the combustion, as a rule, similar to that in which they affect the reserve of heat in the heated layer, which characterizes the combustibility.

In reference to specific conditions of the combustion there are desirable, however, methods of the direct determination of combustibility, especially as not in all conditions do the ability of the conversion to self-propagation and easiness of its excitation prove to be identical.¹

One of such methods is the determination of the minimum pressure (or weight) of the igniter, which provides under definite conditions the combustion of the charge of the explosive tested. In the experiments of V. M. Rogozhnikov² a pressed charge of an explosive

¹Let us recall that with an increase in the density of powerful explosives the detonation ability increases (the critical diameter decreases), and the sensitivity to detonation does not increase but decreases.

²It is possible to carry out ignition at a constant increase pressure, as was done by L. V. Dubnov, and as a measure of combustibility take that value of indicated pressure starting from which the ignition leads to combustion.

was placed in a manometric bomb, and the minimum charge of the igniter (mixture of pyroxylin and ammonium nitrate 1:1), at which combustion occurred was determined. Table 48 gives the results of these experiments. In the second graph in parentheses the corresponding pressures of the combustion of the igniter was shown.

Table 48. Combustibility of some explosives, according to experiments in a manometric bomb.

(Charges without a shell, weight of charge, 4 g, diameter, 20 mm, the igniter - mixture of pyroxylin and ammonium nitrate 1:1.)

Explosives	Minimum charge of igniter, g (pressure, at)	Time of the achievement of the maximum pressure, ms	Maximum pressure, at
A. Density of charge 0.95-0.99 from the specific gravity of the explosive			
Potassium picrate	0,2 (25)	110	520
62% dynamite		180	710
Tetryl		280	816
Ammonium perchlorate	0,4 (55)	750	286
Xylol		750	570
Trotyl	0,6 (85)	580	720
Trinitrobenzene		520	870
Ammonium picrate		500	770
Trinitroaniline		570	810
Rock ammonite		290	770
Ammonite 6 ZhV	1,0 (140)	590	646
Ammonite PZhV-2G		520	440
Ammonite No. 8		520	400
Ammonite No. 6		720	660
Ammonal VA-4		760	664
Mixture AN with TNB*		650	765
Mixture AN with TNA*		510	680
Mixture AN with TNK*		720	575
Ammonium nitrate	2,0 (360) (extinguish- ment of com- bustion)		

B. Density of the charge 0.75 from specific gravity of the explosive

Trotyl	0,4 (55)	370	720
Ammonite No. 6	0,8 (115)	680	720

*Mixtures of ammonium nitrate with trinitrobenzene, trinitroaniline and trinitroxyline of the composition ~3:1.

The given tables show that of the number of explosives studied, the greatest combustibility is characterized by 62% gelatin-dynamite and potassium picrate, and the least by ammonium nitrate. They show also that under conditions of these experiments combustibility usually increases with a decrease in density. The pressure of the igniter necessary for combustion decreases with an increase in the surface of the ignited charge - the combustion of the latter along the large surface prevents a drop in pressure because of the removal of heat into walls of the bomb.

The catalytic additions to the ammonium nitrate increases its combustibility.

Other methods of the estimation of combustibility were also used. Thus, G. N. Besspalov studied the combustibility of powders at atmospheric pressure, placing a column of explosive on the end of the charge of large diameter of the power, which possesses small critical diameter of combustion.

The minimum diameter of the igniting charge was determined, in other words, the diameter of the hot "spot" induced on the end of the ignited charge, at which combustion of the latter occurs. Between the diameter of the "spot" and the critical diameter of combustion for different powders a definite conformity was observed. With the increase in pressure the rate of the combustion of different powders increases unequally; correspondingly the relationship in critical diameters can be different at increased pressures than at atmospheric pressure.

Pokhil [266] studied the combustion of powders by radiant energy. Used as a source of light was an arc lamp, the radiation of which was focused with the help of two paraboloidal reflectors. The density of the radiant energy in the focal body was determined calorimetrically. Used as the criterion of combustibility of the powder was the minimum quantity of heat (in cal/cm^2) which had to be imparted to it for combustion. The calculation of this quantity was produced taking into account the reflection factor of the powder. Some results of experiments are given in Table 49. The table shows the pyroxylin powder will be ignited considerably easier than

nitroglycerine, which is connected with the considerably greater transmittance of the latter. Because of this the absorbed radiant energy is distributed in a thicker layer, and the attainable temperature proves to be lower. This explanation is confirmed by the powerful increase in combustibility with an admixture to the powder of carbon black (0.5%), which decreases its transmittance tens of times. The combustibility of such a powder becomes more than that of pyroxylin. On the other hand, the admixture of carbon black to pyroxylin powder practically does not decrease its low transmittance and is weakly reflected in the combustibility.

Table 49. Combustibility of powders by radiant energy depending on the powder type, the state of the surface and the form of the specimens.

Powder	Form of the powder and state of the surface	Thermal impulse	Absorbed part of thermal impulse	Reflection factor, α (approximately)
		cal/cm ²		
Nitroglycerine (N)	Cylinder, smooth surface.....	8.2	6.56	0.2
"	Cylinder, end surface is cut into square with a side of ~2mm and depth of 1 mm; surface is dusted.....	5.0	4.5	0.1
"	Cylinder, end surface is cut into squares with a side of ~2mm and depth of 1 mm; surface is not dusted.....	3.5	3.15	0.1
"	Cylinder, surface which was formed with discontinuity of the powder.....	5.3	-	-
	Ball, smooth surface.....	9.1	7.28	0.2
Nitroglycerine (N) + ~0.5% carbon black	Cylinder, smooth surface.....	3.2	2.72	0.15
The same	Cylinder, end surface is cut into squares with a side of ~2mm and depth ~1 mm; surface is dusted.....	2.5	2.37	0.05
	Cylinder, smooth surface.....	3.1	2.63	0.15
Nitroglycerine (N) + 3% carbon black				
Pyroxylin	Cylinder, smooth surface.....	5.0	3.0	0.4
"	Cylinder, on the end surface small dents are made.....	3.0	2.4	0.2
"	Ball, smooth surface.....	5.6	3.36	0.4
Pyroxylin + ~0.5% carbon black	Ball, smooth surface.....	4.0	3.2	0.2
Pressed pellet (95% nitroglycerine + 5% carbon black)	Cylinder.....	0.89	0.85	0.05

With a rough surface receiving the radiation, the powder will be ignited easier partly in connection with the fact that in this case the reflection factor decreases, and partly because of the fact that the projections and edges will be ignited generally easier: the relationship of the heat arrival and of heat removal from them is more favorable than that for smooth surface. The pressed pellet of nitroglycerine powder with 5% carbon black requires for combustion several times less radiant energy than that of the solid charge. Combustibility also depends on the form of the charge - a ball will be ignited with more difficulty than will a cylinder on its end.

Conclusions

With the intense heating of an explosive from the surface, upon the reaching on the latter of a certain critical temperature, which represents for volatile explosives the boiling point and for nonvolatile explosives - the temperature of gasification, vapors or gaseous products of initial dissociation are formed. These vapors are rapidly heated to the temperature of spontaneous ignition, and combustion of the explosive begins. If at this moment the heated layer of the condensed phase corresponds to the layer which is available during steady combustion, then combustion starts and proceeds at a constant rate. If the indicated layer is thinner or thicker than the "steady" one, then combustion in the beginning proceeds accordingly slower or faster than does steady combustion. The time of normal inflammation corresponds to the time of the heating necessary for the formation of "steady" heated layer.

The measure of combustibility of an explosive can be the heat reserve in the heated layer during steady combustion. The more the necessary quantity of heat, the less the combustibility. Theory indicates that the heat reserve in a heated layer during steady combustion is directly proportional to thermal conductivity, and with a difference of temperatures - critical and initial, - it is inversely proportional to the rate of combustion and, consequently, to the pressure.

Experimental methods of the determination of combustibility should be based on the determination of the heat reserve necessary for the exitation of normal combustion. The comparative estimate of combustibility can be performed also from the magnitude of the critical diameter of combustion, the minimum pressure of products of combustion of the igniter necessary for combustion of the explosive in a closed volume, and also according to the size of the center of high temperature sufficient for the exitation of combustion.

III. Distribution of Combustion on the Surface of a Charge

With the ignition of a charge of an explosive on a certain small part of its open surface, combustion in many cases is more rapidly propagated along the surface of the charge than into the depth of the substance. This can lead to the fact that the charge, ignited at one point of its surface, is rapidly encompassed with a flame and burns over the entire surface from the periphery into the depth of the charge. Such a pattern of the process is observed, for example, with the ignition of the charge of tetryl and some other explosives in the air. Occurring outwardly similar is combustion with the combustion of the powder charge in a closed or semiclose volume, for example, in a firing weapon.

The high rate of the surface propagation of the flame during combustion in air is usually connected with that fact that in all the explosives studied a reaction during combustion under atmospheric pressure does not occur up to the end, and combustible gases even in substances with a zero oxygen balance, for example, nitroglycol, are formed. With combustion in air these gases, mixing with it, burn up to the end, which leads to the considerable increase in temperature. Thus, the surface layers of the charge along the circuit of the front of combustion are heated by gases of higher temperature than the surface layers of the central part of the cross section of the front of combustion. It is natural therefore, that the first layers burn faster.

The fact that the surface propagation of the flame at high speed is connected in the case of smokeless powders, namely, with secondary reactions, which occur upon contact with the air, follows from experiments [267], which indicated that in inert gas both rates - surface combustion and combustion into the depth of the charge - are equal. More than that, even with combustion in air under conditions when a secondary flame is absent, the surface propagation of combustion does not take place [268]. This conclusion is confirmed also by the fact that the magnitude of the rate of the surface propagation of the flame is much more in substances with a great oxygen deficiency, which form during the combustion of many combustible gases able then to burn upon contact with the air.

Thus, with the combustion of the pressed tetryl, the rate of which is equal to 0.047 cm/s, the rate of the surface propagation of combustion reaches 1.70 cm/s; in exactly the same manner in nitroglycerine powder the rate of combustion along the surface is 2.78 cm/s, and with the rate of combustion into the depth - 0.075 cm/s; at 62% dynamite - a substance with an excess in oxygen, which has a rate of combustion approximately twice greater than that of tetryl, the rate of the surface propagation of the flame is much less than that in tetryl.

A known role in the process of the surface propagation of the flame at considerable rates of combustion can also be played by a certain increase in pressure, which is formed in the front of the combustion. Under the effect of this elevation in pressure gases can be propagated in different directions, including along the surface of the charge, causing its combustion. The assumption was made that with the surface propagation of combustion in the air, the arrival of energy due to radiation can be important. If this was so, then the rate of combustion into the depth of the grain should have been increased. Direct experiments indicate that the effect of radiation of the secondary flame of nitroglycerine powder on the rate of its combustion, to a noticeable degree, does not take place [269]. With the combustion of cylinders of powder in air the rate of combustion is 0.0797 cm/s, and with combustion in a current of carbonic acid,

when a secondary flame is not formed - 0.0765 cm/s. With combustion of a cylinder of powder in air, but without an asbestos winding, the rate of combustion, calculated according to the surface rate and angle of a cone, is 0.0747 cm/s.

The high rate of the propagation of combustion on the surface during combustion in a closed volume has another reason. The pressure during combustion increases, gases being formed during the combustion rapidly fill the free volume of the combustion chamber, displacing and compressing that air which was found in it with the simultaneous mixing with this air. The gases have a high temperature and heat the surface of the powder, which leads to its combustion.

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